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**ADATECHNOLOGIES, INC**

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**Army/SBIR Phase I Final Report**

**Army Grant No. DAAL03-90-C-0023**

**Development of a Portable, Fast  
Response Tracer Analysis System  
for Concentration Fluctuation  
Measurements**

ADA Report No. 27291F01

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**Development of a Portable, Fast Response Tracer Analysis System for  
Concentration Fluctuation Measurements**

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13. ABSTRACT (Maximum 200 words)  Concentration fluctuation field experiments performed to date have lacked data pertaining to very short-term changes in tracer concentration. This type of information is critical when a dispersing plume contains toxic or flammable compounds. Therefore, a device capable of very fast response (5 to 10 Hz), measuring the tracer material with high sensitivity, portability, and ease of use is desired.  The initial design concept of the tracer analyzer involved sampling by venturi aspiration and measurement by electron-capture detector. After considerable testing and replacement of components, it was determined that the venturi system was not feasible for measuring SF <sub>6</sub> in air. A new tracer analyzer design was described, in which an oxygen-removal system is incorporated in a field-portable unit. The concept of the new design has been proven in commercial fast-response SF <sub>6</sub> analyzers.				
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## I. EXECUTIVE SUMMARY

The primary objective of the Phase I research and development effort was to determine the feasibility of an electron-capture detector-based tracer analyzer that does not utilize an oxygen removal system to measure  $\text{SF}_6$  in air. The secondary objective was to demonstrate the ability of the new tracer analyzer to measure  $\text{SF}_6$  with the sensitivity and response speed required for concentration fluctuation field experiments. The innovative concept in this program was to use a venturi aspirator to dilute ambient oxygen to approximately 1% to avoid interference with the  $\text{SF}_6$  measurement. The venturi would also provide a means to sample the air without the use of a pump.

The design goals for the  $\text{SF}_6$  analyzer included: 1) measurement of  $\text{SF}_6$  in air down to 200 ppt, 2) response frequency in the range of 5 to 10 Hz, 3) calibration stability over 90-minute period, 4) ability to combine components in small sampling head, and 5) continuous operation in a stand-alone mode.

The results of the Phase I study showed that measuring  $\text{SF}_6$  at ppt levels cannot be done in the presence of oxygen, even after dilution. Based on the Phase I results, the following conclusions can be made regarding the  $\text{SF}_6$  device:

1) **The venturi flow system successfully diluted and transferred an air sample to the ECD.** In Task 1, the venturi was designed, fabricated, and calibrated over a range of nitrogen flows expected to be used during the study. The dilution ratios (nitrogen flow to orifice flow) were in the target range for diluting the air sample.

2)  **$\text{SF}_6$  was measured when the pure gas was injected near the venturi orifice.** The measurement of  $\text{SF}_6$  by the ECD was optimized in Task 3 in this manner. However, adjusting the ECD pulse conditions did not result in a clear identification of the best  $\text{SF}_6$  signal.

3)  **$\text{SF}_6$  was measured at 32 ppb with the venturi sampling system.** Using the venturi sampling system in Task 4, 32 ppb appeared to be the limit of detection for  $\text{SF}_6$  in the presence of 0.6% ambient oxygen.

4) **A tracer analyzer that utilizes an oxygen-removal system can be modified for concentration fluctuation field experiments.** A new portable  $\text{SF}_6$  analyzer design was proposed in Task 5.

## II. ACKNOWLEDGEMENTS

The author of this report would like to recognize the valued assistance provided by several individuals who contributed to the Phase I research effort. They include:

- o Mr. Richard Benner, a consultant on the project who conceived the idea of the portable SF<sub>6</sub> analyzer.
- o Mr. John Frame, for providing equipment and expertise on tracer gas measurement.
- o Mr. James Butz, who designed the dilution venturi and created the model for the venturi flows.
- o Ms. Sharon Sjostrom, who created the drawings in this report.
- o Drs. David Hyatt and James Armstrong, for providing guidance during this project and for their valuable editorial comments.
- o Ms. Sarah Hix, for assisting in the preparation of the final report.

Finally, the author would like to thank Dr. Walter Bach, the technical monitor for this project, for visiting ADA Technologies and providing valuable technical direction for the Phase I effort and information regarding the Army's requirements for the SF<sub>6</sub> device.

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## VI. PHASE I RESEARCH PROGRAM

### A. INTRODUCTION

On a battlefield, there are circumstances in which it is desirable to be able to predict the atmospheric dispersion and transport of an air mass. For example, the movement of a smoke camouflage is critical from both an offensive and a defensive standpoint. The movement of an air mass which contains chemical or biological warfare agents is of extreme importance. Also, the ability to predict the movement of an air mass surrounding a munitions storage facility is of considerable interest. Therefore, the U.S. Army is interested in developing the capability to predict atmospheric dispersion through concentration fluctuation studies. These studies require multipoint sampling with a high sampling frequency in order to obtain the resolution necessary to observe the extremely short-term concentration excursions. It is therefore desirable that the monitoring device be both fast-responding and inexpensive. The results of these studies would provide data for modeling dispersion in the boundary layer ( $\leq 1$  kilometer) over distances of 2 to 20 kilometers.

In the past, the Army has used oil fog releases and one-second-averaged concentrations obtained with aerosol photometers (Hanna, 1986). This technique apparently worked well, but was limited to short-range transport (less than 100 meters) and tests of only 6 minutes duration.

#### Army Requirements for Concentration Fluctuation Measurements

In order to improve the quality of data collected in concentration fluctuation field experiments, a small, inexpensive, fast response device for measuring a tracer gas such as sulfur hexafluoride ( $\text{SF}_6$ ) is needed. The device should be capable of measuring both the mean and fluctuating concentration of the tracer material as far as 5 km from the source. The response frequency of the instrument should be in the range of 5 to 10 Hz. The instrument must be portable enough to mount on masts to heights of 30 meters, and must not interfere with the air flow containing the tracer material. The instrument must be capable of being calibrated in the field, and hold its calibration for 90 minutes. Since the field experiments could be carried out in a wide range of environments, the instrument must be tolerant of extreme heat, extreme cold, dust and smoke. Finally, the instrument should be battery-powered, and be able to log data and transmit the data to a remote site via telemetry, if possible.

ADA Technologies, Inc. (ADA) is developing a portable, fast response analyzer that could be used to measure the fluctuating concentration of  $\text{SF}_6$  in tracer studies conducted at Army research and development facilities. The  $\text{SF}_6$ -sensing element is the electron-capture detector, not only because of its proven sensitivity, but also because of its selectivity, which reduces the problem of interferences. The final instrument will be robust,

simple to operate and calibrate, and will not interfere with air flows containing the SF<sub>6</sub> tracer.

## B. BACKGROUND

### 1. Concentration Fluctuation Measurements

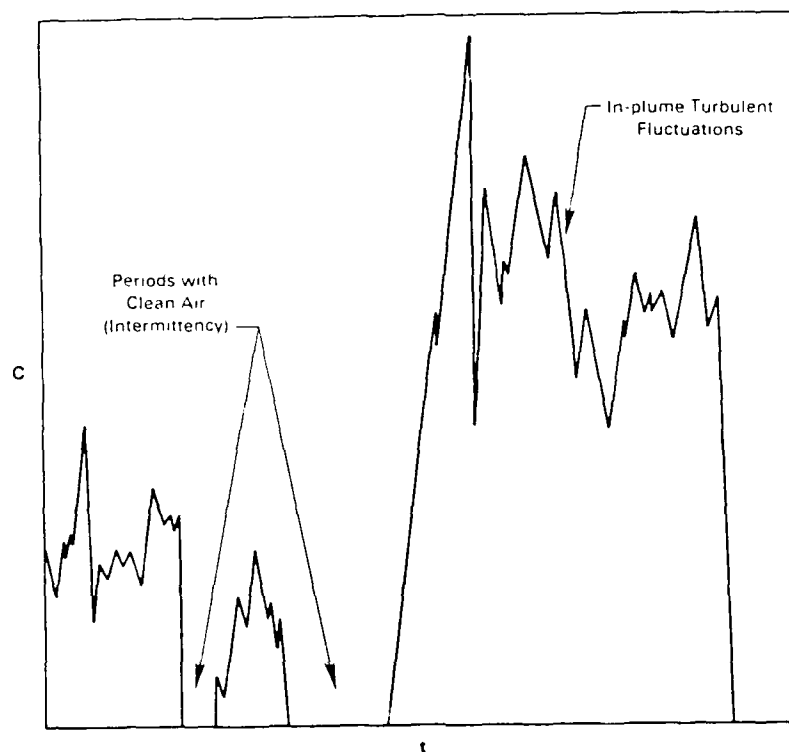
Meander and internal turbulence are the two major processes that produce concentration fluctuations observed at a fixed receptor in a diffusing plume (Peterson et al., 1988). The meandering component is caused by atmospheric eddies which exceed the dimensions of the plume. The result is a horizontally-moving plume which is slowly moved across a receptor. The concentration fluctuations caused by plume meander are characterized by time scales on the order of tens to hundreds of seconds. Atmospheric turbulent eddies with dimensions comparable to those of the plume contribute to concentration fluctuations on time scales of sub-second to tens of seconds. These fluctuations are caused by entrainment of "clean" air from outside the plume into the plume volume (Figure 1). As even smaller turbulent eddies work to homogenize the concentration within the plume, the plume grows in radial dimensions.

Interest in the characteristics of short-term concentration fluctuations has increased for plumes of toxic or flammable materials (Peterson et al., 1988). A time-averaged concentration of a gas will not adequately address whether or not a flammable condition exists during short time intervals. This is because large instantaneous deviations in the concentration occur as the plume moves over a receptor. The same is true for the release of toxic vapors in which the short-term concentration excursions (less than one second in duration) can be critical in determining toxic exposure (Hanna, 1984).

Concentration fluctuation experiments have been rare and have, by necessity, been carried out on a very limited scale since instrumentation with adequate sensitivity and response speed is very expensive and difficult to use.

Only a few field experiments have been performed that specifically address concentration fluctuations within a turbulent diffusing plume. Early attempts at collecting such data included krypton-85 releases with Geiger counters as samplers (Ramsdell and Hinds, 1971). The concentration of krypton-85 was averaged over 38.4 seconds by 63 samplers, and tests of 10 to 20 minutes were typically performed. The release of a radioactive gas, combined with the relatively long averaging time of the samplers, makes this technique undesirable.

Other concentration fluctuation experiments have been carried out in laboratory convection tanks (Deardorff and Willis, 1984) but suffer from uncertainties related to how well the atmosphere is simulated by the tank. Although laboratory experiments are a valuable tool, their results must be validated by field measurements.



**Figure 1. Example of Concentration Fluctuations Within a Diffusing Plume. The abscissa shows an arbitrary time scale and the ordinate is the concentration of the plume species. (From Hanna, 1984).**

## 2. The Use of Tracers

Certain inert compounds can be released in the atmosphere to determine the transport and dispersion of an air mass. The inert compounds are known as tracers. Tracer compounds are typically released at a known rate and measured at various distant locations. Tracers are measured either by collecting samples of the air for later analysis, or by directly analyzing the air on a real-time basis. Being relatively unreactive compounds, tracers can be measured many miles from the release site. By knowing the release rate of the tracer material, it is possible to calculate the dilution of the tracer. In addition, the continuous measurement of the tracer material provides highly-resolved data pertaining to the fluctuating concentration of the tracer, thus providing information on the physical processes leading to dispersion in the atmosphere.

The advantages of measuring a tracer compound instead of more reactive gases of interest include: 1) high sensitivity of measurement techniques for tracers; 2) the ability to measure the unreactive tracers many miles from the release site, since they are not affected by chemical conversion; 3) greater ease of measuring a single tracer compound as opposed to several gases which may or may not be measurable at atmospheric concentrations; and 4) the tracer species is non-toxic. In many research field programs, the release and measurement of a tracer gas concurrently with a gaseous species of interest provides information regarding the emission rate and atmospheric lifetime of the compound.

Although smoke and fluorescent particles have been used as tracers to some degree, problems of sensitivity, complex analysis, and loss to surfaces have prevented their widespread use (Niemeyer and McCormick, 1968; Pasquill, 1983). The use of halogenated compounds as tracers began in 1966. These compounds included sulfur hexafluoride ( $\text{SF}_6$ ), bromotrifluoromethane ( $\text{CBrF}_3$ ), and octafluorocyclobutane ( $\text{C}_4\text{F}_8$ ). In addition to being inert, colorless, odorless, non-toxic, and non-adsorptive to surfaces, these halogenated species are easily measured at low part-per-trillion (ppt) levels by electron-capture detector (ECD) instrumentation. Of these three compounds,  $\text{SF}_6$  has gained the widest use because of its low cost, ease of sampling and analysis, and very low detection limit with ECD measurement.

## 3. Electron-Capture Detection of Halogenated Tracers

In order to understand why the ECD is the prevalent detector in tracer instruments, it is necessary to understand the theory of operation of the ECD. The ECD consists of an electron source, an anode, a cathode, and an electronics package. The electron source, usually a small solid-state radioactive source, provides a constant flow of beta particles which bombard the carrier gas. The beta particles strip electrons from the carrier gas and produce a cloud of thermal electrons of constant number density (Figure 2a). Positive ions are also produced in this process. When a potential is applied, the thermal electrons are collected at the anode, producing a standing current. When an electron-absorbing species such as  $\text{SF}_6$  enters the ECD,  $\text{SF}_6$  reacts with the thermal electrons in the following manner:

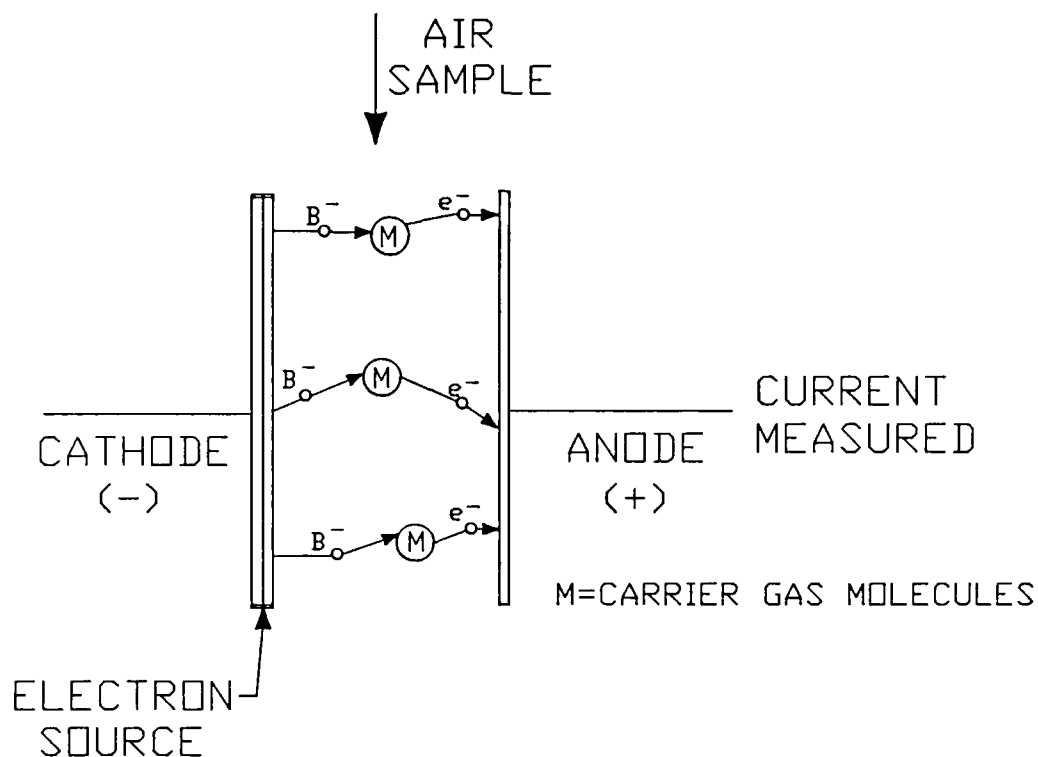


Figure 2a. Operation of the ECD with no electron-capturing compound present.

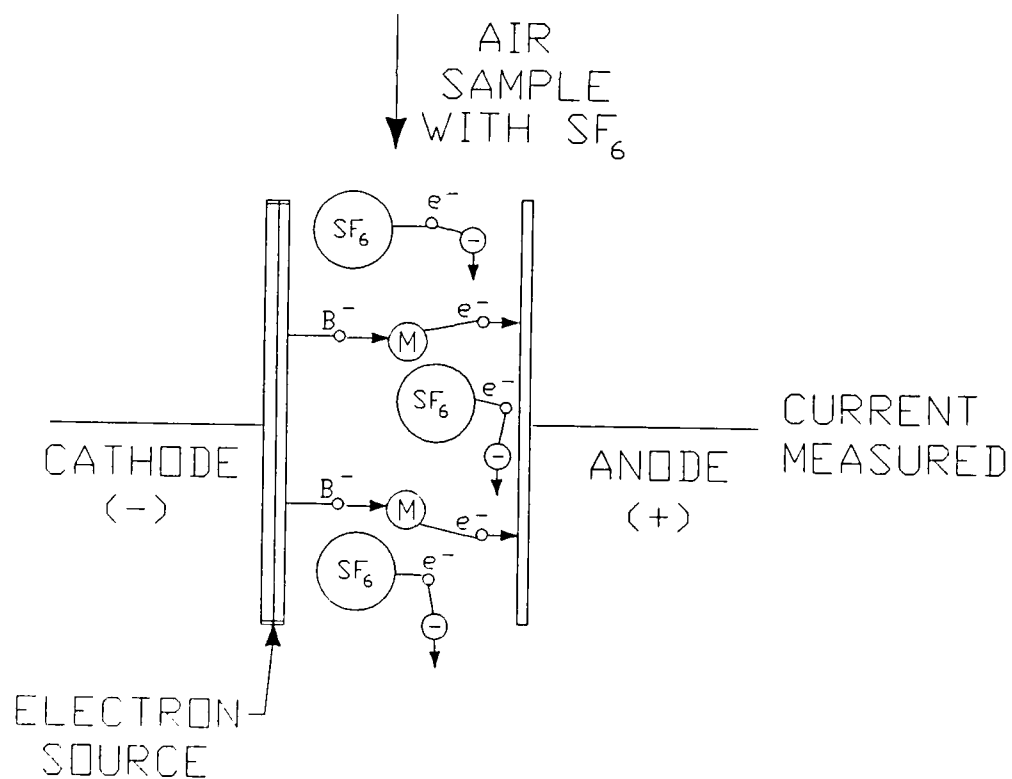


Figure 2b. Operation of the ECD with  $SF_6$  Present.



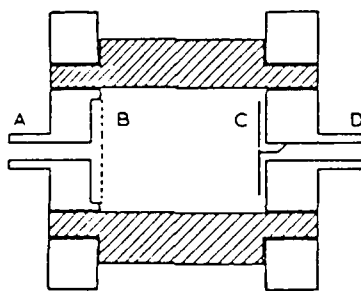
Because the negatively-charged species have greater mass than the electrons, the negative ions will drift more slowly toward the anode than the electrons. Thus, the negative ions are swept out of the ECD cell before reaching the anode (Figure 2b). The concentration of electrons in the ECD, and therefore the standing current, is reduced. This signal is processed by the ECD electronics such that the current decrease is observed as an increase in the signal voltage.

The ideal electron source should produce a large baseline current with a minimal noise level. An alpha-emitting source (e.g., americium-241), with an energy output of 5.4 million electron volts (MeV), produces a large baseline current, but also high detector noise. Low-energy beta-emitters with high specific activities, primarily nickel-63 (0.067 MeV) and tritium (0.018 MeV), provide large currents with minimal detector noise. The beta sources, which are essentially the only sources used in ECDs today, also provide the least radiation hazard. Nickel-63 is used preferentially in applications requiring the ECD to be heated to 400°C. However, its higher-energy beta emissions create a higher noise level and less sensitivity than the lower-energy tritium beta emissions. Tritium is available in the form of a scandium or titanium tritide.

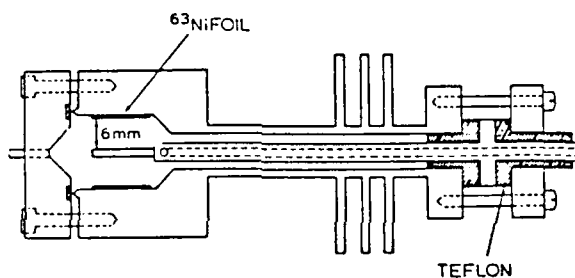
The dimensions and geometry of the ECD cell are extremely important parameters because they affect the distribution and flow of electrons in the ECD and therefore the characteristics of the current and resulting signal for the species of interest. Three different cell designs are commonly used (Poole and Zlatkis, 1981): 1) the parallel plate, 2) the coaxial cylinder, and 3) the asymmetric or displaced coaxial cylinder. These cell configurations are shown in Figure 3 (from Poole and Zlatkis, 1981). The parallel plate ECD (Figure 3a) is the simplest design, and permits the position of the source and anode to be varied as necessary for improved performance. In the coaxial cylinder configuration (Figure 3b), the source foil is wrapped around the inside the cell, maximizing the source area. The cell itself serves as the cathode, and the axial anode extends into the center of the cell. The coaxial design is preferred for nickel-63, which has a lower specific activity than tritium. The results obtained using tritium in either the parallel plate or coaxial cylinder configurations are the same. The asymmetric configuration (Figure 3c) differs from the other two designs in that the cathode is separated from the anode by a glass, ceramic, or Teflon insulator. If the inter-electrode distance is maximized, then the applied electric field is longitudinally asymmetric. This results in the electron cloud concentrating around the anode, and prevents the buildup of positive ions at the cathode.

The volume of the ECD cell should be as small as possible in order to maximize the source area-to-cell volume ratio. This is more easily accomplished with the lower-energy tritium source. The higher source area-to-cell volume ratio of the coaxial ECD produces a higher baseline current and therefore greater sensitivity than with other cell designs.

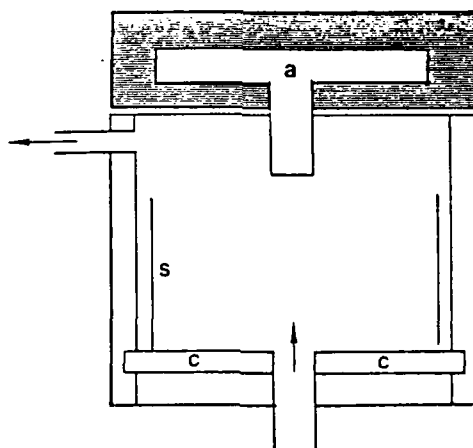




**Figure 3a. Parallel plate electron-capture detector; showing (A), the carrier gas inlet and anode; (B), the diffuser; (C), the electron source; and (D), the carrier gas outlet and cathode.**



**Figure 3b. Coaxial cylinder electron-capture detector with a nickel-63 electron source.**



**Figure 3c. Asymmetric electron-capture detector, also known as the pin-cup ECD. (a) is the anode, (c) is the cathode, and (s) is the source.**

The ECD is normally operated in one of three modes (Poole and Zlatkis, 1981): the constant potential mode, the pulsed potential mode, and the constant current mode. The pulsed potential mode offers several advantages over the constant potential and constant current modes, including superior linearity, decreased complexity, and lower cost of the components.

In the pulsed potential mode, the application of a voltage pulse prevents the buildup of positive ions at the cathode by allowing time for the carrier gas to sweep the positive ions out of the ECD between pulses. As a result, all electrons are collected at the anode during the pulse, and allowed to reach thermal equilibrium between pulses. The duration (width) of the pulse and length of time (period) between pulses, as well as the magnitude of the potential (pulse amplitude), can be adjusted to maximize the collection of electrons, but minimize the collection of negative ions. This results in an improved signal-to-noise ratio for the electron-capturing species of interest.

#### **4. Development of the Continuous Tracer Analyzer**

The most quantitative and fastest-responding technique for concentration fluctuation measurements using a tracer gas is real-time, continuous monitoring of the halogenated tracer with an ECD-based instrument. All continuous tracer analyzers in use today are based on an instrument concept introduced by Simmonds, Lovelock and Lovelock in 1976. The flow diagram of the Simmonds, Lovelock and Lovelock, or SLL, instrument is shown in Figure 4. In order to measure ppt-level concentrations of tracer gas in air, oxygen, a weak electron absorber, must be removed from the air stream. This is accomplished by catalytically reacting the ambient oxygen with hydrogen to produce water vapor. Interfering compounds such as chlorofluorocarbons (CFCs) are also destroyed in this reaction, but  $\text{SF}_6$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and perfluorocarbons pass through. The water vapor is removed in a drier before the air sample enters the ECD for analysis.

Although this technology appears to be straightforward, most attempts to operate the continuous analyzer in field experiments have been unsuccessful. The most significant improvement in the original SLL instrument design has been the introduction of the Nafion countercurrent drier in instruments developed by Lamb (1980), Baxter (1982), and Lee (1984). However, none of these continuous analyzers have performed reliably enough to be used routinely for concentration fluctuation studies.

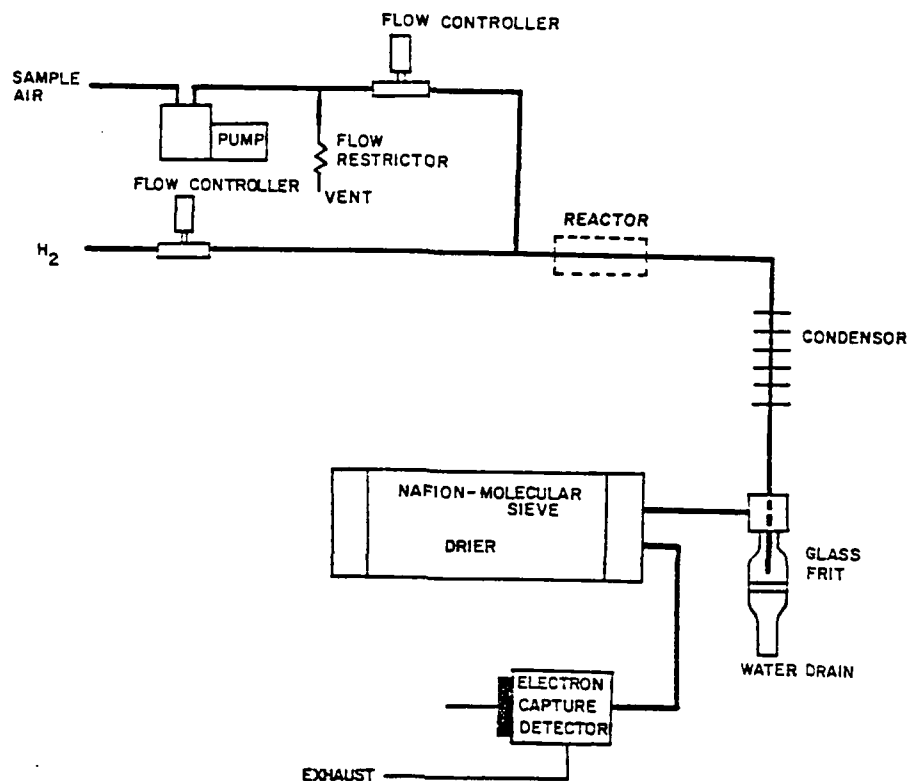


Figure 4. Basic flow diagram of the Simmonds, Lovelock, and Lovelock continuous analyzer design (Lamb, 1980).

### 5. Improvement of the Continuous Tracer Analyzer

An improved, fast-response version of the original SLL analyzer was developed by Benner and Lamb (1985). The Benner/Lamb continuous analyzer features improved dependability, increased precision, less dependence on environmental factors, and significantly faster response and delay times than previous instruments. The response time is defined as the time required to see a change in voltage from 0% to 63% of the maximum signal caused by an instantaneous increase in SF<sub>6</sub> concentration at the instrument inlet. The delay time is the time between the introduction of the sample and the first perceptible change in voltage.

A schematic diagram illustrating the details of the Benner/Lamb analyzer is shown in Figure 5. The major difference between this instrument and other continuous analyzers is the placement of the sample pump and flow controller. In this analyzer design, the pump and flow controller are placed after the ECD in order to minimize the dead volume upstream of the detector and therefore minimize response and delay times of the analyzer. Also, the placement of a surge tank between the pump and flow controller serves to dampen flow pulsations, but does not affect the response and delay times.

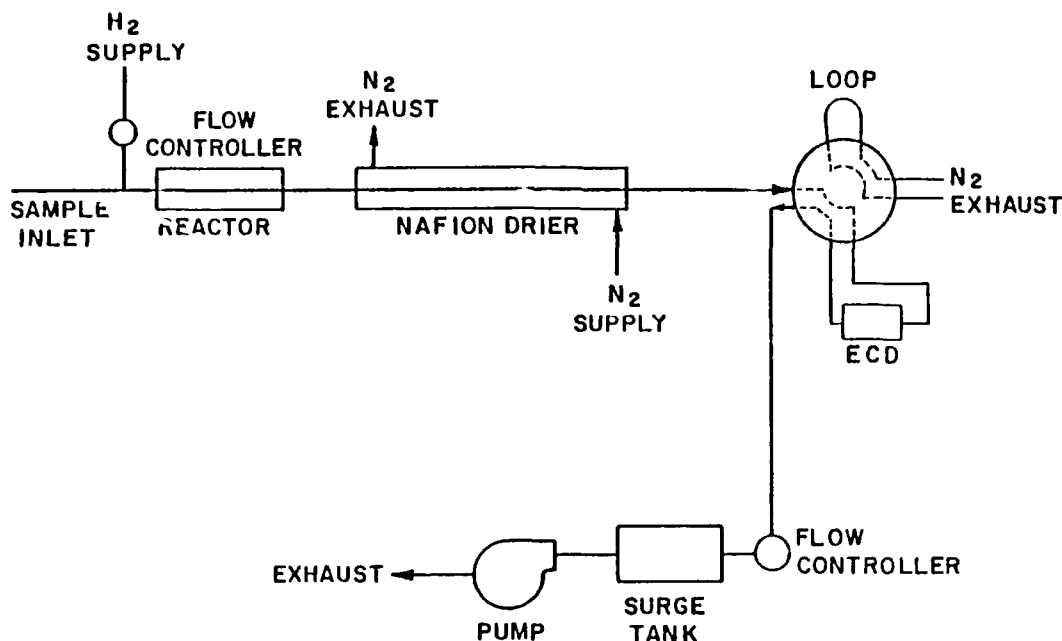


Figure 5. Flow diagram of the Benner/Lamb continuous tracer analyzer (Benner and Lamb, 1985).

Benner and Lamb (1985) have compared the performance characteristics of the different continuous analyzers in use today. The most significant breakthrough made by the Benner/Lamb analyzer is improved response and delay times. This instrument has also demonstrated improved dependability over other analyzers. Because the response time of this continuous analyzer is 4 to 30 times faster than that of other analyzers, this analyzer can be used to measure concentration fluctuations that are 4 to 30 times shorter in duration than those measured by other analyzers.

Laboratory performance tests with the Benner/Lamb continuous analyzer showed that the instrument gave a reproducible response to  $\text{SF}_6$  concentrations in the range of 38 ppt to 1015 ppt over one month of continuous operation which included exposure to temperatures ranging from  $4^\circ\text{C}$  to  $40^\circ\text{C}$ . In fact, further experiments with the analyzer have demonstrated that the instrument calibration changes less than 10% over periods longer than a year. A field calibration performed outdoors, in which 3  $\text{SF}_6$  standards (40, 82, and 680 ppt) were injected every hour for over 50 hours, yielded equally reproducible results. Thus, the capability of operating the instrument in the field, without sacrificing precision, was demonstrated. The baseline drift rate, which was also measured during the outdoor experiment, was found to be only 3 ppt/min. This rate represents a change in the baseline signal of less than 0.1% of full scale response per minute, and would not interfere with most field measurements.

Although this continuous analyzer would meet the required program specifications of fast response, sensitivity, and ruggedness, the instrument is expensive (\$18K), complex, and large. A simpler tracer analyzer design that would meet the Army's requirements for portability as well as response time, sensitivity, and ruggedness at a lower cost than the Benner/Lamb instrument is clearly needed.

## 6. An Alternative Method for Measuring SF<sub>6</sub> in Air

The most complex part of the continuous analyzer is the oxygen removal system, which includes the catalytic reactor and dryer. The ratio of hydrogen flow to sample flow and the temperature of the reactor must be carefully adjusted in order to initiate and maintain the oxygen/hydrogen reaction. At the same time, the temperature of the product gas stream from the reactor must be kept below 220°C or damage to the Nafion dryer will result. If the Nafion dryer is not working properly, the water produced from the oxygen/hydrogen reaction will enter the ECD, causing damage. Thus, several critical parameters must be controlled simultaneously during startup of the continuous analyzer.

Using a venturi aspirator to draw a sample stream into a carrier gas would result in the dilution of the ambient air to a level where oxygen might not interfere with the measurement of the tracer gas. Although measurements of certain chlorinated hydrocarbons with the ECD have shown a response enhancement due to 0.2% oxygen, the effect of oxygen on the ECD response to SF<sub>6</sub> had not been determined. If SF<sub>6</sub> could be detected at reasonably low concentrations (e.g., 200 ppt) in the presence of approximately 1% oxygen, then the obvious advantage of the venturi aspirator would be the elimination of both the catalytic reactor and the dryer. In addition, there would be no need for a pump, since the venturi would also be providing the means for sample introduction, and the elimination of the pump would significantly decrease the power requirement for the instrument.

## 7. Venturi Aspirators

Venturi aspirators are commonly used to provide both the vacuum source and mixing system for dilution systems. Venturi tubes are the union of a converging section (nozzle) and a diverging section (diffuser) separated by a short throat section. The purpose of the venturi tube is to create a region of low static pressure, produced by the accelerating flow at the venturi throat. The mass flow rate through a venturi tube can be predicted by the following equation for compressible subsonic flow (Blevins, 1984):

$$m(t) = C d^{2/4} \{ 1/[1-(d/D)^4] \}^{1/2} [2 \text{ Rho}(P_1 - P_2)]^{1/2} Y \quad (3)$$

where:

$m(t)$  = Mass flow rate, g/s

$C$  = Discharge coefficient

$d$  = Throat diameter, cm

$D$  = Upstream diameter, cm

$\text{Rho}$  = Gas density at diameter  $D$ , g/cm<sup>3</sup>

$P_1, P_2$  = Static pressure at diameter  $D$  and throat, dynes/cm<sup>2</sup>

$Y$  = Expansion coefficient

As can be seen from this equation, the vacuum produced by the venturi (i.e.  $P_2$ ) can be increased by either increasing the mass flow rate or decreasing the throat diameter. This provides a great deal of versatility in designing a venturi because it can be built to satisfy criteria for both the vacuum required and the flow rate desired.

In constructing venturi tubes, considerable precision must be used in machining the throat sections. For optimal performance, the throat should have minimal surface roughness. In addition, the vacuum tap should be drilled perpendicular to the nozzle axis with openings into the flow that are sharp and free of burrs.

In addition to providing a good method for sample extraction, venturis produce excellent mixing of components due to the high velocity in the throat. Figure 6 is a plot of measured dilution rate versus calculated dilution rate for a three-stage dilution system built by Durham (1983). The calculated dilution rate was based on flow measurements through the venturis and the sample ports. The measured dilution rate was based upon a known input concentration of  $\text{SO}_2$  and a measurement of the diluted concentration. The measurements were made immediately downstream of the venturis. The one-to-one correspondence of this plot over three orders of magnitude demonstrates that essentially complete mixing is produced by the aspirators.

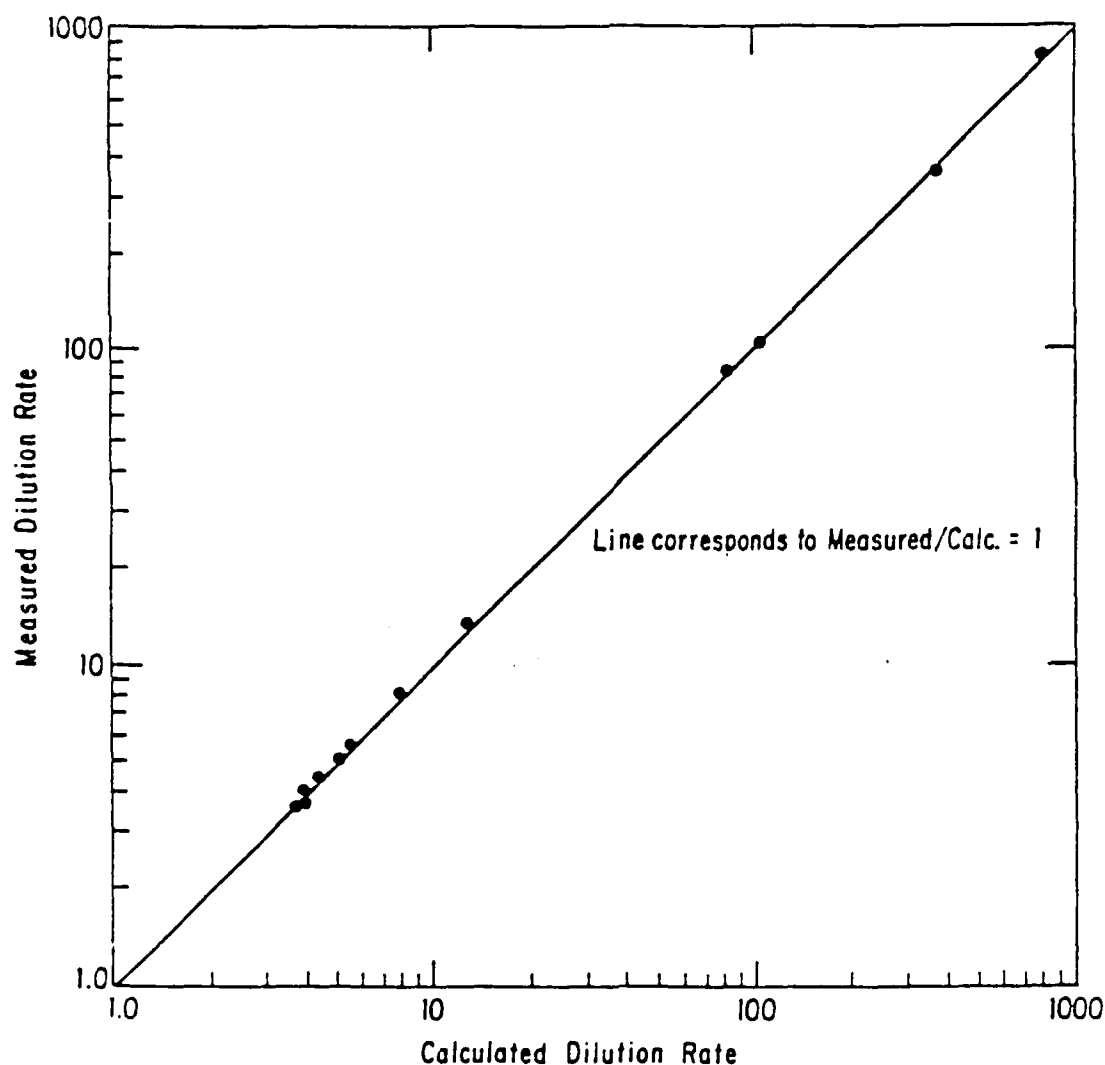


figure 6. Dynamic calibration of a three-stage dilution system (Durham, 1983).

## VII. PHASE I TECHNICAL OBJECTIVES

The primary objective of the Phase I research and development effort was to design, fabricate, and test a prototype tracer analyzer that can provide accurate concentration fluctuation measurements. The sensing element for the system is the ECD, which has been used in all continuous tracer analyzers. The device would be designed such that the size and cost are minimized to meet the need for a large number of sensing devices that can be mounted on masts and do not disturb the air flow containing the tracer compound. The Phase I prototype would be thoroughly tested in the laboratory to determine response time, calibration reproducibility, and baseline drift.

The proposed field design for the tracer analyzer included two sections: one section was to consist of a sample head which included the venturi and ECD, and one section was to contain the electronics for the ECD.

The Phase I objectives were addressed by five tasks. In Tasks 1 and 2, the venturi flow system, ECD, and electronics were to be designed and assembled. The ECD and flow system were to be optimized for measuring  $\text{SF}_6$  in the presence of oxygen in Task 3. In Task 4, a complete  $\text{SF}_6$  calibration was to be performed, and the stability of the calibration checked over a 90-minute period. The response time of the device was also to be determined in this task. Necessary modifications to the prototype system for Phase II were to be recommended in Task 5 based on the results of the laboratory experiments.

## VIII. PHASE I RESULTS

The design of the ADA tracer analyzer, as presented in the Phase I proposal, involved sampling by venturi aspiration and measurement of the tracer gas by electron-capture detection. A flow diagram of this system is shown in Figure 7. Nitrogen as the carrier gas passed through the venturi at a controlled rate. The vacuum resulting from the rapid flow of nitrogen through the venturi throat drew ambient air at a known flow rate through an orifice. The air sample in the nitrogen was partially vented before passing into the ECD for measurement of the  $\text{SF}_6$  concentration. The sample stream flow through the ECD was controlled at about  $100 \text{ cm}^3/\text{min}$  by adjusting the vent flow. The  $\text{SF}_6$  in the sample stream was detected as a net change in current (nanoamps), as measured by a Keithley picoammeter (Aztec Enterprises, Inc., Denver, CO), and converted to voltage, which was measured on a Linseis strip chart recorder (Cole-Parmer Instrument Co., Chicago, IL) as millivolts.

A discussion of the selection and testing of the flow system components is presented below.

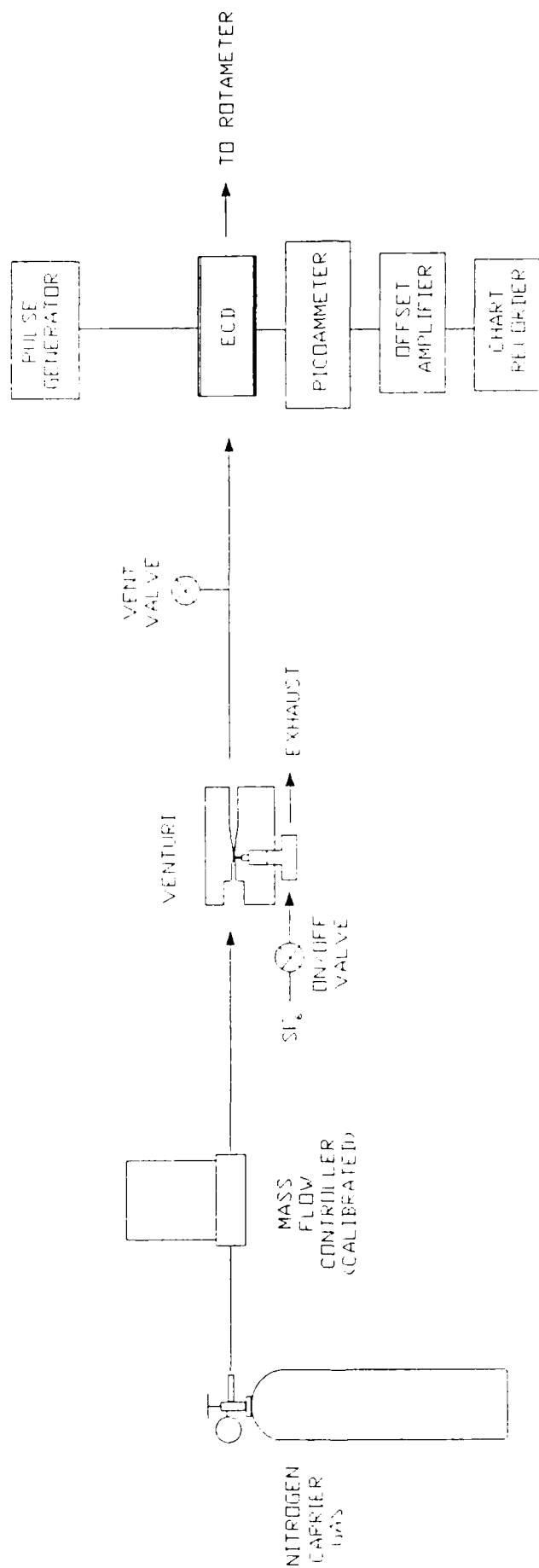


Figure 7. Flow diagram of the venturi/ECD tracer analyzer.



## A. ASSEMBLY OF THE VENTURI FLOW SYSTEM

The proposed innovative concept of the tracer analyzer was the use of a dilution venturi aspirator (Figure 8). As stated above, the venturi served two purposes: 1) to draw in the air sample, and 2) to dilute the ambient oxygen to a level that would not interfere with the measurement of  $\text{SF}_6$  by the ECD. Ultra pure nitrogen carrier gas was passed through the venturi, with the flow regulated by a mass flow controller. The nitrogen flow controlled both the direction (positive or negative) and the magnitude of the flow through the inlet orifice due to the difference between the pressure at the venturi inlet and the pressure in the venturi throat ( $\Delta P$ ). Of course, a negative orifice flow was desired for drawing the air sample into the nitrogen carrier stream and to the detector.

### 1. Design of the Venturi

The important factors which were considered when designing the venturi included 1) minimizing the nitrogen flow rate in order to conserve the cylinder gas, 2) creating enough vacuum in the venturi throat to draw in the sample air, even in the presence of strong ambient winds, 3) providing a nitrogen-to-sample air dilution ratio which would sufficiently dilute the oxygen concentration while providing a high enough concentration of  $\text{SF}_6$  to be measurable by the ECD, 4) fabricating the venturi inlet so that different-sized sample orifices could be easily switched for testing, and 5) choosing a venturi orifice diameter that was small enough to achieve the desired dilution ratio but large enough that dust particles would not clog the orifice during field experiments.

In order to reduce the oxygen concentration of the air sample to 1% or less, at which oxygen was expected to minimally affect the ECD sensitivity, the dilution ratio of nitrogen flow to sample air flow must be at least 20:1. The venturi dimensions were calculated based on this ratio, an estimated 1000  $\text{cm}^3$  per minute (ccm) nitrogen flow, and a venturi throat pressure of 4 inches of water below ambient pressure. The material of choice for the venturi was aluminum because of its ease of manufacture, the need for tight tolerances on the dimensions, and its relative inertness to  $\text{SF}_6$ . In order to test different orifice sizes, the venturi inlet would be threaded, and the actual orifices would be screws drilled out to the desired diameters that could be interchanged as necessary.

### 2. Calibration of the Venturi

In order to predict dilution ratios over a wide range of nitrogen flows using a spreadsheet model, it was necessary to determine the venturi and inlet orifice discharge coefficients. The data needed to calculate the discharge coefficients were obtained by varying the nitrogen flow from 667 ccm to 2689 ccm, measuring the temperature and pressure at the venturi inlet, measuring the pressure at the throat, and measuring the orifice flow rate (for the orifice calibration). All flows were measured using a bubble flow meter, the temperature was measured using a type K thermocouple, and pressures were measured using two different water manometers. The venturi orifice diameter tested--0.008 in--was the value calculated using the specifications described above for the venturi

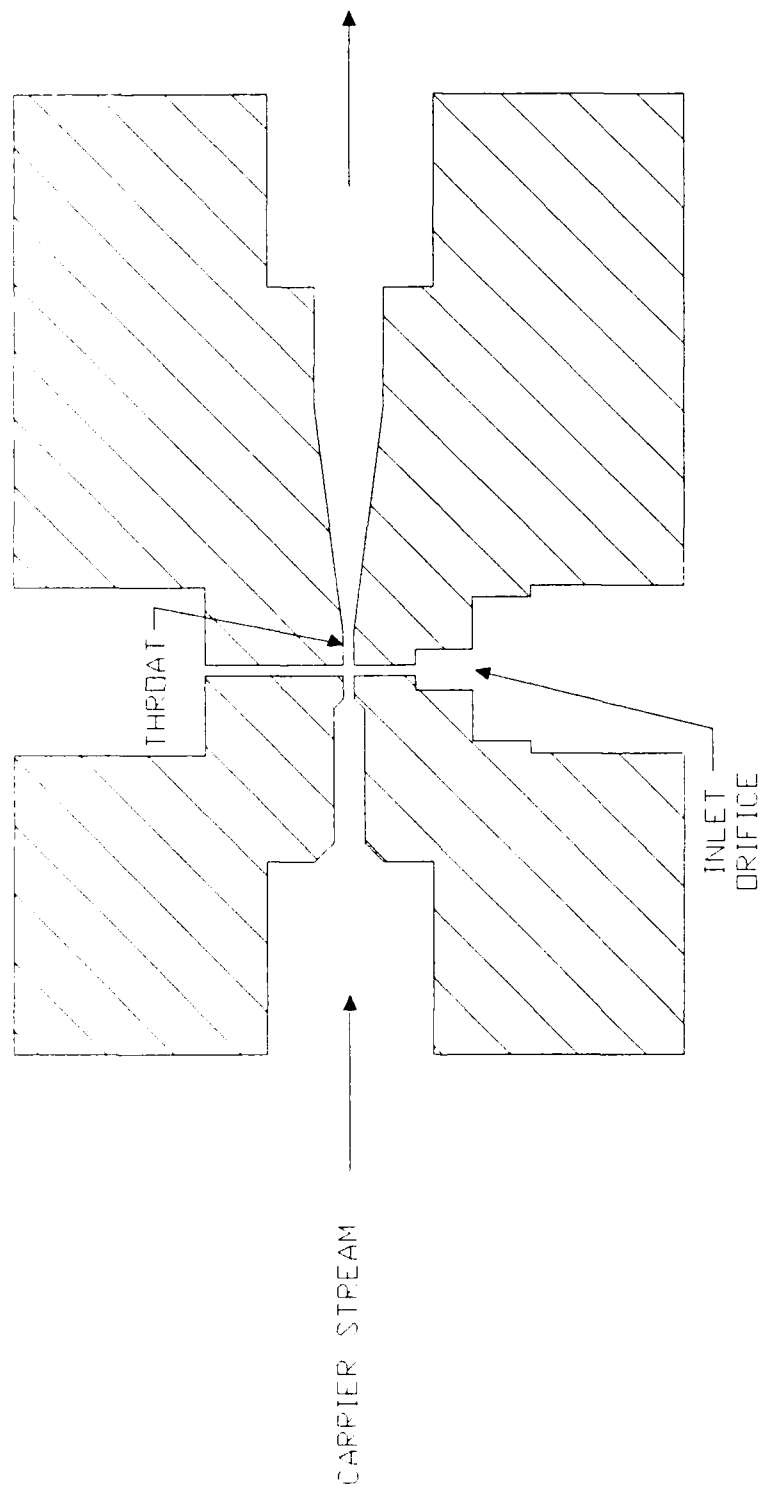


Figure 8. Schematic diagram of the venturi aspirator.

design. The data are shown in Tables 1 and 2. At nitrogen flows of 667 and 1328 ccm, the orifice flow was in a positive direction, but the orifice flow became more negative as the nitrogen flow rate increased. In addition, the dilution ratio decreased gradually from 39:1 to 28:1 between nitrogen flows of 2006 and 2689 ccm.

**Table 1. Venturi Calibration with Orifice Plugged**

<u>Nitrogen flow</u> <u>cm<sup>3</sup>/min</u>	<u>Entrance pressure</u> <u>in. of mercury</u>	<u>Throat pressure</u> <u>in. of mercury</u>	<u>Temperature, °F</u>
673	2.75	0.16	75
1331	8.25	0.14	76
2016	15.25	-2.20	78
2460	20	-5.92	76

**Table 2. Orifice Calibration**

<u>Nitrogen flow</u> <u>cm<sup>3</sup>/min</u>	<u>Orifice flow</u> <u>cm<sup>3</sup>/min</u>	<u>Entrance pressure</u> <u>in. of mercury</u>	<u>Throat pressure</u> <u>in. of mercury</u>	<u>Dilution</u> <u>Ratio</u>
667	+6.7	2.7	0.09	----
1328	+2.7	8.5	0.05	----
2006	-51.0	15.3	-1.97	39
2472	-83.9	20.7	-4.48	29
2689	-97.2	24	-5.84	28

These results were incorporated in the spreadsheet model. The model results for the 0.008-in orifice and for two larger orifice diameters are shown in a plot of nitrogen flow rate versus dilution ratio in Figure 9. These plots were generated using a discharge coefficient of 0.885, which was obtained using the orifice calibration data (Table 2). The three dilution ratios from Table 2 fall close to the 0.008-in orifice curve, particularly at the higher nitrogen flows. As shown in the figure, the model predicts that the dilution ratio decreases sharply between nitrogen flows of 1740 and 2055 ccm. Due to the sensitivity of the dilution ratio to the nitrogen flow--as well as positive orifice flow--at the lower nitrogen flows, the nitrogen flow rate must be greater than about 2000 ccm.

### 3. Effect of Dust on Venturi Operation

Following the calibration of the venturi, a brief experiment was performed to determine the effect of dust on the orifice flow rate. This experiment was performed because the tracer analyzer will be operated in dusty environments, and must therefore be capable of operating satisfactorily under such conditions. The venturi was placed in a 5000

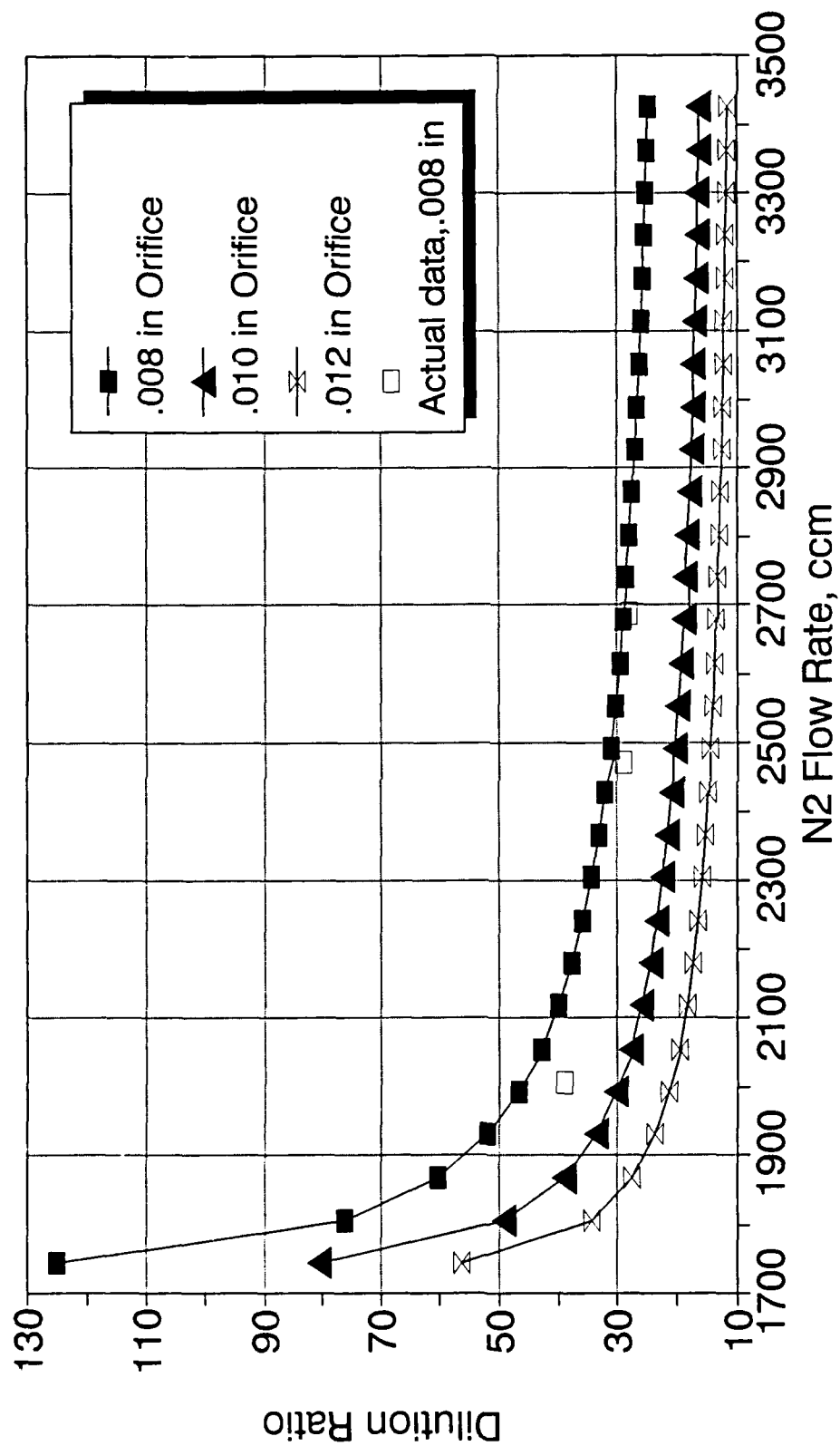


Figure 9. Dilution rates for venturi with .008, .010, .012 inch orifices.

cm<sup>3</sup> test chamber with nitrogen flowing through it at a rate of 2645 ccm. Very fine coal fly ash was placed inside the box, and a fan served to suspend the ash. Over a three-hour test period, the flow through the orifice decreased from 89 ccm to 60 ccm. Although the orifice did not plug completely during the test, this flow decrease would change the dilution ratio from 30 to 44, which would significantly change the SF<sub>6</sub> signal. Therefore, a filter would most likely be placed over the inlet orifice in the field instrument.

## **B. DESIGN AND FABRICATION OF PROTOTYPE TRACER ANALYZER**

The basic experimental setup for the tracer analyzer is shown in Figure 7. The nitrogen flow was set at 2645 ccm for most of the Phase I experiments, resulting in a negative orifice flow rate of 85 ccm and a dilution ratio of 31. The flow through the ECD, controlled by adjusting the vent valve upstream of the ECD, was about 100 standard ccm. As shown in the figure, the air sample containing SF<sub>6</sub> was passed through a tee connected to the inlet orifice at a rate of approximately 130 ccm, and the venturi vacuum served to draw the sample into the nitrogen stream. The ECD current was converted to voltage and displayed on a strip chart recorder. The ECD/electrometer detection system was modified during Phase I to a more compact design, as described later.

The ECD used in the Phase I work was fabricated in-house, and had a coaxial cylinder geometry (Figure 10). The basic ECD design comprised a 1.5-cm<sup>2</sup> titanium tritide foil wrapped inside a 0.48-cm diameter brass compression fitting union, which served as the ECD cathode. A 0.32-cm copper tube inserted in the middle of the union was the anode. The anode was sealed at the end facing the flow of air, but notches in the anode at the opposite end allowed the air to flow out of the ECD. The inlet tubing through which the sample air entered the ECD was inserted through the union to be as close to the anode as practical without touching it. The volume of the cell was approximately 100 microliters, with an anode-cathode separation of 1.65 millimeters. There was no temperature control on the ECD, and it was therefore operated at ambient temperature.

Throughout the Phase I study the tracer analyzer was modified as necessary to improve the SF<sub>6</sub> sensitivity, response time, etc. The stainless steel fittings and tubing between the venturi and the ECD were as short as practical in order to achieve the fastest response time. The ECD itself was modified by replacing the brass union and copper anode with all stainless steel parts. The cathode was drilled out to a 0.64-cm diameter to increase the anode-cathode separation. Before reinserting the tritium foil, the cathode and foil were scrubbed to eliminate contaminants that could contribute to a high background signal. The picoammeter was replaced by a faster current amplifier, and the ECD and current amplifier were enclosed in a box to further eliminate noise in the ECD signal.

## **C. OPTIMIZATION OF ECD AND FLOW SYSTEM FOR THE MEASUREMENT OF SF<sub>6</sub>**

A Hewlett Packard 214B Pulse Generator was employed during the Phase I study to provide a pulsed potential source for the ECD. The pulse conditions (amplitude, period and width) were varied to identify the optimum parameters for measuring SF<sub>6</sub>. The pulse

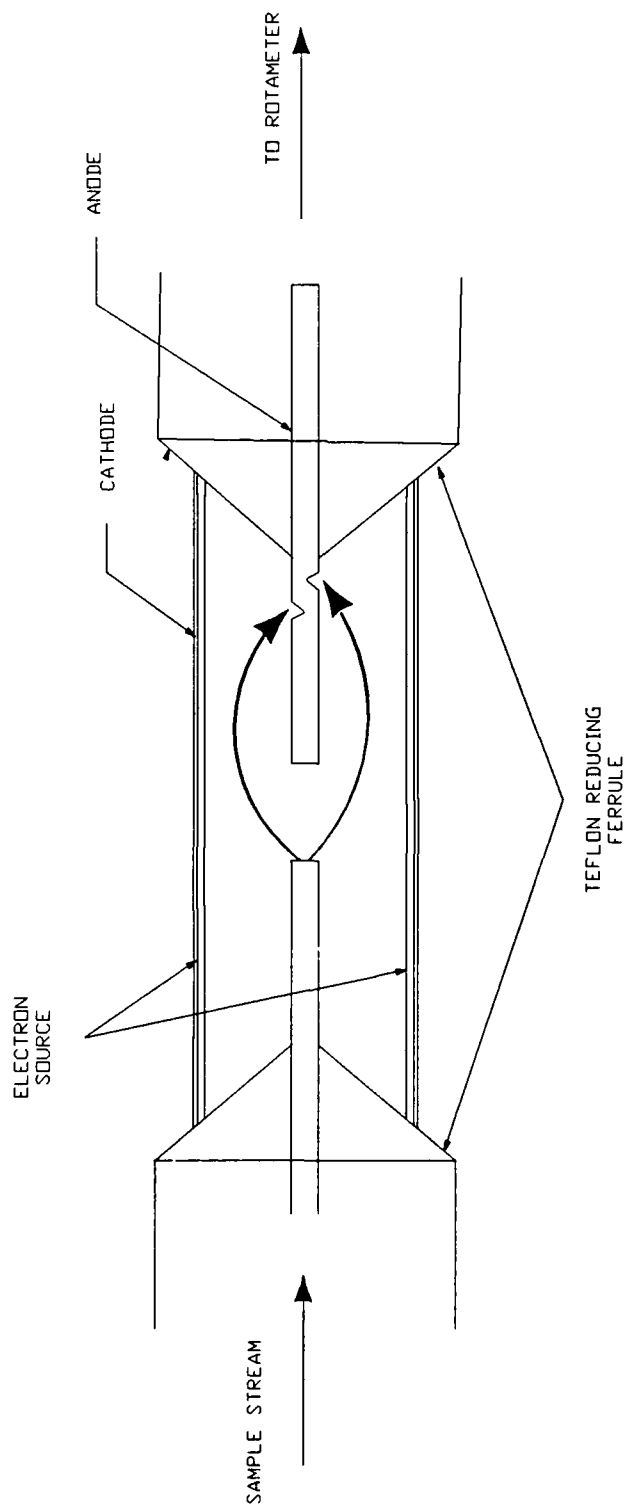


Figure 10. Tritium ECD fabricated in the laboratory.

generator output waveforms were displayed on an oscilloscope to verify the pulse settings. The pulse conditions which are typically used for a nitrogen carrier gas are -30 volts amplitude, 0.05-0.5 milliseconds (ms) period, and 0.0005-0.001 ms width. The procedure used for identifying the optimal pulse conditions involved holding one or two pulse variables constant while adjusting the others. The "optimum" pulse settings are considered those which give the largest signal-to-noise ratio for an SF<sub>6</sub> signal.

The prototype tracer analyzer (Figure 7) was used to introduce SF<sub>6</sub> to the ECD in the initial pulse tuning experiments. Later experiments were performed without the venturi in the flow system. Certified SF<sub>6</sub> standards (air balance) in the range of 95.5 parts per trillion (ppt) to 103.5 parts per billion (ppb) were analyzed with the venturi in place by switching the flow of the standard on and off. When the SF<sub>6</sub> flow was off, the venturi would draw in room air as the background through the open end of the orifice tee. Although a "signal" was observed when SF<sub>6</sub> was flowing through the system, this signal was actually a shift in the ECD baseline current caused by the difference between the balance air in the SF<sub>6</sub> standards and the room air. This baseline shift was due to either water vapor differences between the two air matrices or contaminants present in the room air which were not present in the standards. Consequently, all SF<sub>6</sub> standards gave the same magnitude "signal".

In order to avoid baseline shifts, it was necessary to provide the same air source for both the background and for the SF<sub>6</sub> diluent gas. This was accomplished initially by filling a 3-cm<sup>3</sup> syringe with pure SF<sub>6</sub> and injecting it near the orifice inlet to the venturi, with room air serving as both the background and dilution gas. The SF<sub>6</sub> response was instantaneous. The next step was to insert a pump, a tee with septum as an injection port, and stainless steel sample cylinder in line to the inlet (Figure 11). While the pump provided a continuous flow of ambient air past the orifice, SF<sub>6</sub> was injected in approximately one-microliter volumes just upstream of the sample cylinder. The purpose of the cylinder was to provide a 300-cm<sup>3</sup> dilution volume, but the air flow was too fast to allow adequate mixing. Therefore, the SF<sub>6</sub> concentration was unknown. The SF<sub>6</sub> signal was again instantaneous using this method of gas introduction.

The pulse conditions were adjusted using this method of SF<sub>6</sub> sample introduction. The results are shown in Table 3. There was surprisingly little variation in the SF<sub>6</sub> signal-to-noise ratio or the baseline current as the pulse conditions were varied over a wide range. The best signal-to-noise ratio (6) was observed at pulse conditions of -30 volts amplitude, 5 ms period, and 1 ms width, which are considerably longer pulses than are typically used in the pulsed potential mode.

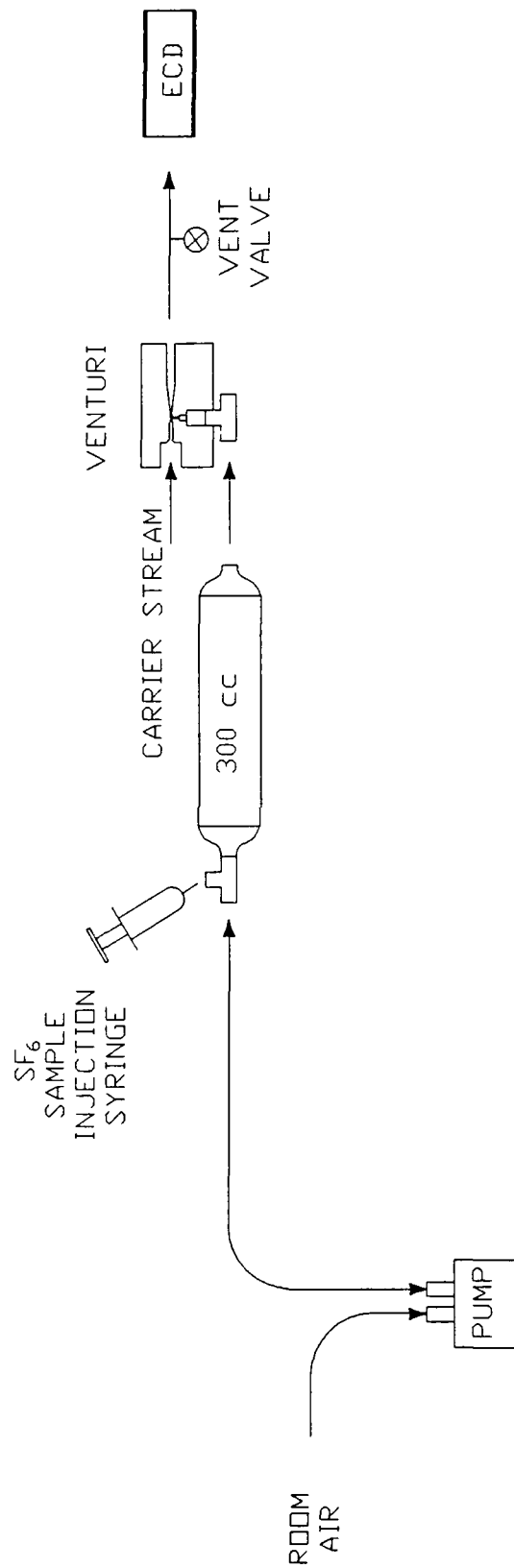


Figure 11. Flow system used to sample SF<sub>6</sub> in pulse-tuning experiments.



**Table 3. Effect of Adjusting Pulse Conditions on the SF<sub>6</sub> Signal-to-Noise Ratio**

<u>Pulse Amplitude</u> (volts)	<u>Pulse Period</u> (microseconds)	<u>Pulse Width</u> (microseconds)	<u>SF<sub>6</sub></u> <u>Signal-to-Noise</u>
-30	10	3	4
-30	50	0.5	4
-30	50	1	3
-30	50	5	4
-30	50	10	2.5
-30	50	14	3
-30	100	0.8	4
-30	100	20	3
-30	500	20	4
-30	500	50	4
-30	500	100	4
-30	200	80	3
-30	2000	100	5
-30	2000	1000	1
-30	5000	1000	6
-60	2000	100	4
-30	100	8	4

The flow rate through the ECD was varied from 29 to 146 standard ccm, but there was no effect on the SF<sub>6</sub> signal.

#### **D. LABORATORY EVALUATION OF THE PROTOTYPE TRACER ANALYZER**

In order to test the speed of the electronics for measuring the SF<sub>6</sub> signal, the flow of the pump air across the inlet orifice of the venturi was varied from 338 ccm to 4800 ccm by adjusting a vent valve placed between the pump and the injection port. With the vent completely closed, the flow of air was 10,000 ccm. The effect of varying the pump flow on the SF<sub>6</sub> signal is shown by the data in Table 4. The SF<sub>6</sub> peak broadened considerably as the flow decreased. The noise fluctuations of 0.3 sec duration were measurable.

**Table 4. Response of ECD as Flow Across Venturi Orifice is Varied**

Pump flow cm <sup>3</sup> /min	SF <sub>6</sub> signal (millivolts)	Width of SF <sub>6</sub> peak (seconds)	Width of noise (seconds)	Noise signal (millivolts)
10,000	18	2	0.3	1.0
4,800	10	5	0.3	0.8
2,700	14	7	---	0.4-0.8
338	29	23	---	1.6

### 1. SF<sub>6</sub> Measurements With and Without the Venturi

A calibrated permeation wafer device (VICI Metronics, Santa Clara, CA) containing SF<sub>6</sub> was obtained in order to measure low concentrations of the gas. The permeation rate was measured by VICI Metronics at 31 nanograms/minute at 30°C; however, the permeation rate was determined to be 18 ng/min at the laboratory temperature.

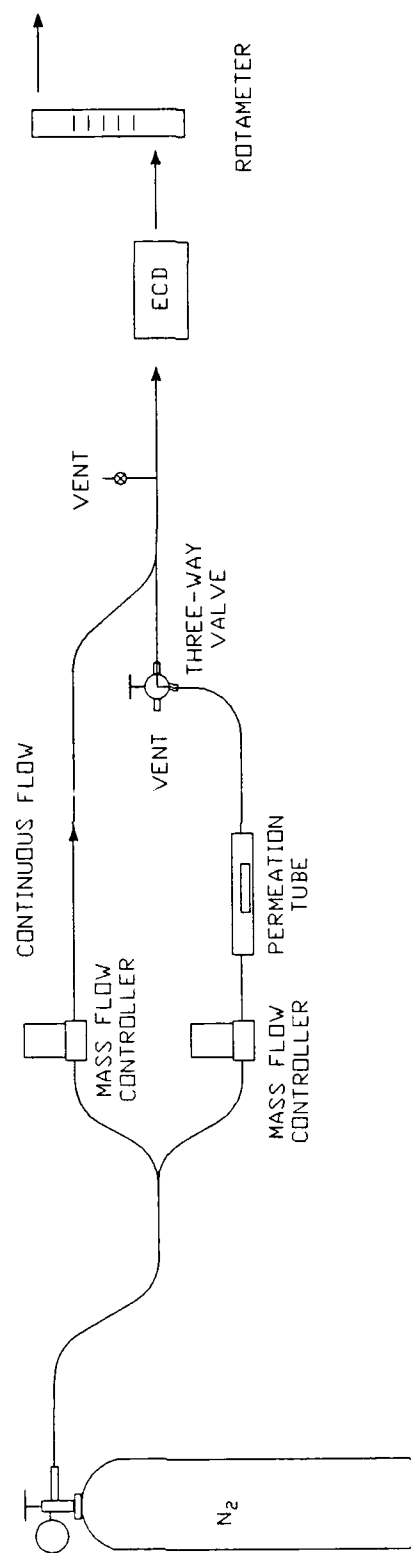
The measurement of SF<sub>6</sub> from the permeation wafer was performed by placing the wafer in a plastic cylindrical container with fittings on each end. Air or N<sub>2</sub> flowed through the container at all times in order to provide a constant rate of SF<sub>6</sub> emission from the permeation device.

The calibration equation for the ECD has the basic form:

$$C = e^{b \cdot R^m} \quad (4)$$

where C is the SF<sub>6</sub> concentration in ppb, b is the y-intercept and m is the slope calculated by regression analysis, and R is the detector response in nanoamps. For the new Keithley current amplifier, which replaced the Model 485 picoammeter, 1 volt was equivalent to 1 nanoamp.

Calibrations were performed without the venturi in line in order to obtain SF<sub>6</sub> data that were not affected by ambient oxygen. The experimental setup is shown in Figure 12. Nitrogen at a flow rate of 10 ccm passed over the permeation device, and this flow was vented to the room except when the three-way valve was switched in-line to the ECD for SF<sub>6</sub> measurement. A second nitrogen flow, serving as a diluent for the permeation source flow, was varied in order to measure SF<sub>6</sub> concentrations ranging from 4.3 to 34 ppb. The calibration curve is shown in Figure 13. The calibration equation was determined to be  $C = 76.3 \cdot R^{1.37}$ , and the correlation coefficient ( $r^2$ ) of the regression was .999. The detection limit was estimated to be 1.4 ppb with a signal-to-noise ratio of 2:1. This concentration is two orders of magnitude higher than the detection limit for commercial SF<sub>6</sub> analyzers.



**Figure 12. Flow system used for  $SF_6$  permeation source calibrations without the venturi in line.**

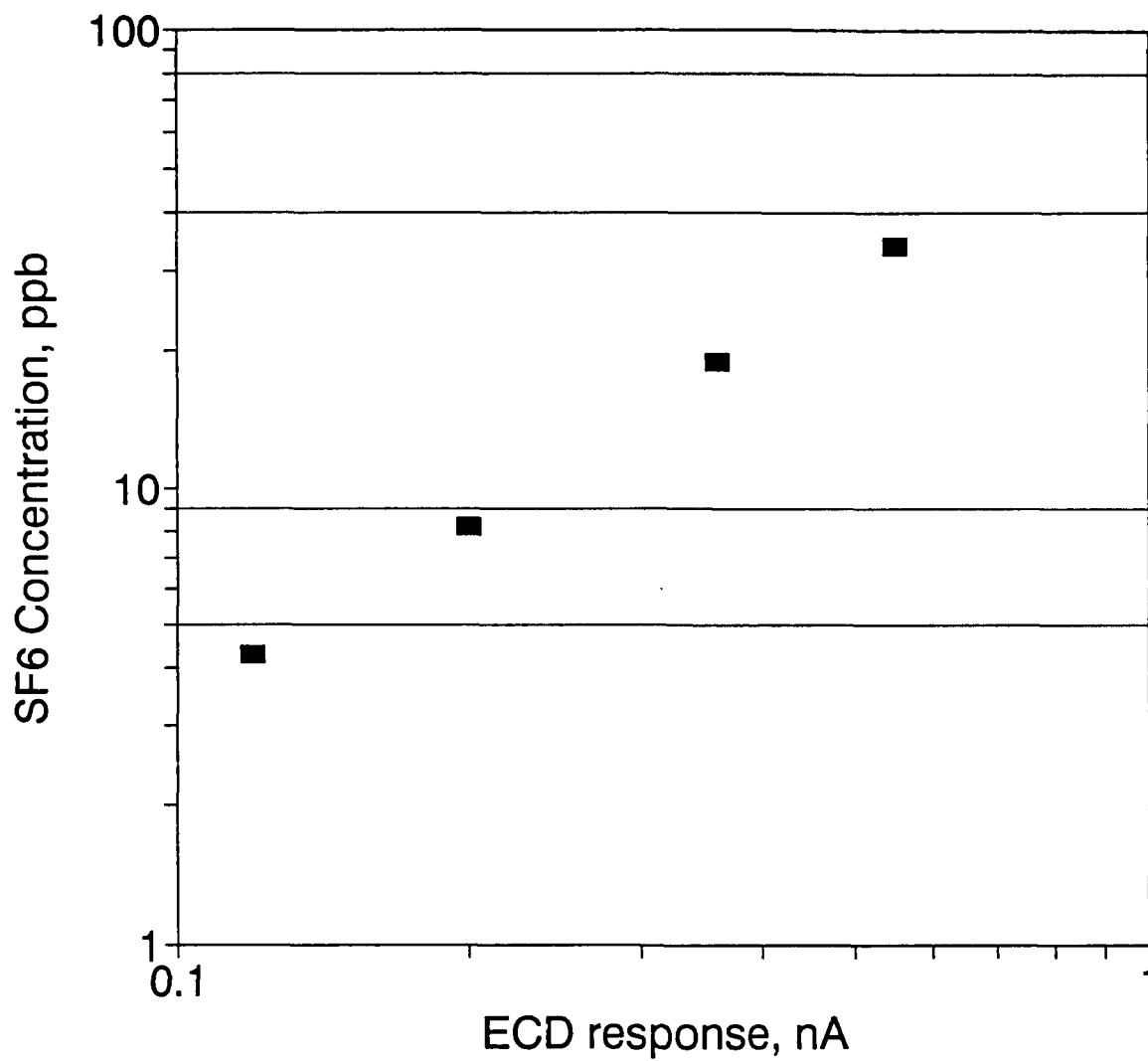


Figure 13. First SF<sub>6</sub> calibration performed with permeation source.

Following this experiment, the venturi was placed in line, and pumped room air at a flow rate of 115 ccm flowed through the inlet orifice tee connected to the venturi. This flow was alternated with 115 ccm of air pumped over the permeation device. The flow setup is shown in Figure 14. The SF<sub>6</sub> concentration was approximately 32 ppb entering the venturi. The resulting signal-to-noise ratio was 1.75:1, so 32 ppb is about the limit of detection for this sampling system.

The ECD and the current amplifier were reassembled in one box at this point in an attempt to decrease the noise level and thereby lower the detection limit. The venturi was reconnected in the flow system, and room air served as both a carrier gas for the permeation device (11 ccm) and a dilution gas for the permeation flow (103 ccm), as in the nitrogen-based flow system shown in Figure 12. The diluted air sample flowed across the venturi orifice inlet. The SF<sub>6</sub> concentration entering the venturi was approximately 33 ppb. Although the noise level was very low (4 millivolts), this concentration was not measured with the venturi flow system.

The venturi was again taken out of the flow system and SF<sub>6</sub> was measured only in the presence of nitrogen. The manual three-way valve was exchanged for a fast solenoid valve (General Valve Corp., Fairfield, NJ) in order to decrease the response time of the SF<sub>6</sub> signal. The output signal was measured on an oscilloscope. This made it possible to adjust pulse conditions and observe the changing signal magnitude without needing to readjust the baseline. The pulse conditions were readjusted to -30 v amplitude, 20 microseconds period, and 0.4 microsecond width for the optimum SF<sub>6</sub> signal.

At the new pulse conditions, a permeation source calibration curve was again obtained, using the flow setup shown in Figure 12, but with the manual three-way valve replaced with the fast solenoid valve. The nitrogen flow was varied, as before, to generate 3 to 12 ppb SF<sub>6</sub> by diluting the 10 ccm permeation source flow. With this calibration, shown in Figure 15, a 600 ppt detection limit (signal-to-noise = 2:1) was achieved. The calibration equation was  $C = 5.68R^{0.66}$ , and the  $r^2$  value was .995. This calibration equation was significantly different from the equation obtained earlier, reflecting the much greater response to SF<sub>6</sub> as a result of the changes described above.

The venturi flow system was again tried, using the pump flow in the same manner as the nitrogen flow. Both 4 ppb and 33 ppb SF<sub>6</sub> concentrations were generated from the flow system, but neither concentration was measured by the ECD. Adjustment of the pulse conditions did not result in the measurement of SF<sub>6</sub>.

Although oxygen was an obvious source of the measurement problems with the venturi flow system, the causes of other problems were also investigated. These problems included: 1) considerable electronic noise, 2) the offset/gain adjustment, and 3) questionable operation of the solenoid valve. Each of these problems were addressed prior to focusing on the oxygen interference.

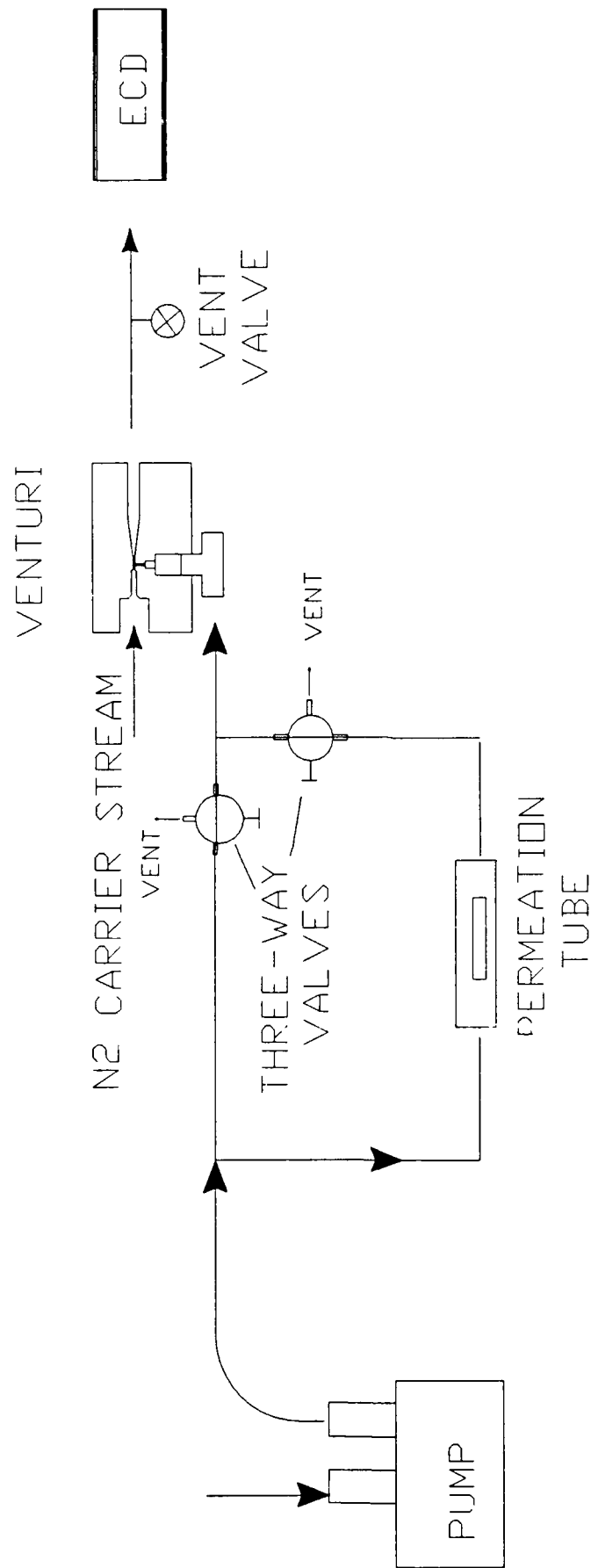


Figure 14. Flow system used to sample  $\text{SF}_6$  from the permeation source. The venturi is in line.

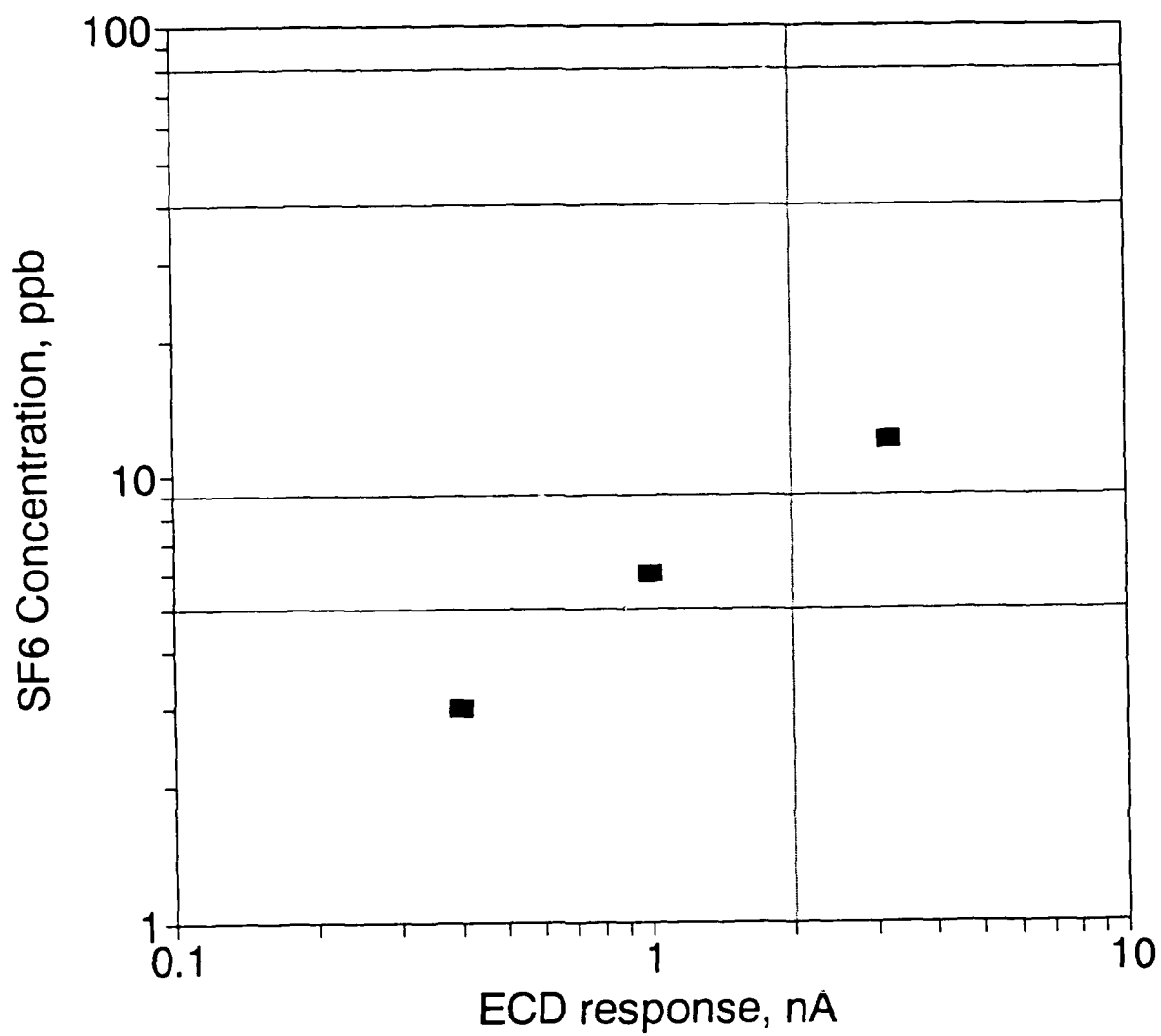


Figure 15. Second SF<sub>6</sub> calibration in nitrogen following changes to the flow system.

## 2. Experiments with a Commercial SF<sub>6</sub> Analyzer

In order to evaluate further the overall performance of the ADA tracer analyzer components, a Precision Tracer Gas Analyzer, #LBF-3 (ScienTech, Inc., Pullman, WA), was obtained. This instrument is the commercial version of the Benner/Lamb continuous SF<sub>6</sub> analyzer (Benner and Lamb, 1985), with an oxygen-removal system consisting of a catalytic reactor and dryer, and with optimized ECD and electronics. The ECD operates at pulse conditions of -30 v amplitude, 150 microseconds period, and 1 microsecond width. Prior to testing the ADA instrument, the LBF-3 was calibrated both with and without the solenoid valve in line (to inject the certified SF<sub>6</sub> standards) in order to check for proper operation and adsorption of SF<sub>6</sub> in the valve. The valve was found to operate properly with no adsorption of SF<sub>6</sub>. Also, the SF<sub>6</sub> permeation device was checked, using the same flow setup shown in Figure 12 and varying the nitrogen diluent flow. The SF<sub>6</sub> permeation rate was verified at  $18 \pm 2$  ng/min.

For the first experiment, the venturi flow system was connected to the LBF-3 ECD, bypassing the catalytic reactor and dryer. A 100 ppb certified SF<sub>6</sub> standard was analyzed using the setup shown in Figure 16. The 100 ppb standard was not detected, even after varying the dilution ratio of the venturi.

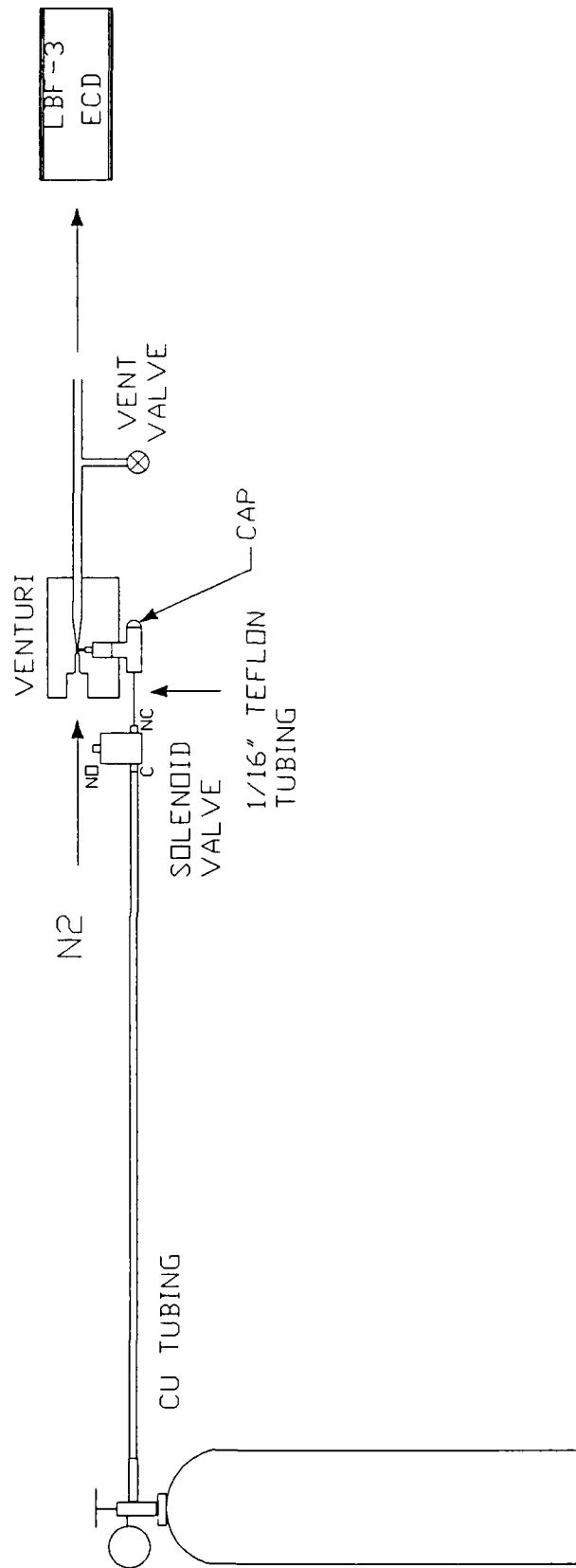
In order to check the venturi, it was connected at the inlet of the LBF-3 analyzer, upstream of the oxygen removal system. Since the sample gas flow was directed through the reactor and dryer, compressed air was substituted for nitrogen as the carrier gas through the venturi. The air flow through the venturi was 2689 ccm and the flow through the inlet orifice was 73 ccm to give a dilution ratio of 39. The solenoid valve injected a 5030 ppt SF<sub>6</sub> standard in the same manner as in the previous experiment. This standard was easily measured, with a signal-to-noise ratio of 39 and an estimated detection limit of 256 ppt. These experiments showed that ambient oxygen, even when diluted to 0.5% levels, prevents the detection of SF<sub>6</sub> with the venturi sampling system.

A few questions remained to be answered regarding the electronics of the ADA system. There was some uncertainty about whether or not the pulse settings were optimum for measuring SF<sub>6</sub> in air. This uncertainty was due to the ability of the ADA detector to measure a lower SF<sub>6</sub> concentration in air (32 ppb) at pulse period of 5 ms and pulse width of 1 ms, than the venturi/LBF-3 setup, which could not measure 100 ppb SF<sub>6</sub> in air (oxygen removal system bypassed) at pulse period of 150 microseconds and pulse width of 1 microsecond. The ADA ECD electronics were also questionable because of the inability to achieve better than 600 ppt detection limit with nitrogen carrier gas.

In order to resolve the uncertainties with the ADA prototype instrument, a second Tracer Gas Analyzer, TGA-4000, was borrowed. The goal was to evaluate the ECD and electronics of the ADA instrument by interchanging with the ECD and electronics of the TGA-4000.

Mr. John Frame, President of ScienTech, Inc. and manufacturer of the Tracer Gas Analyzer, provided guidance during the evaluation experiments because of his expertise with ECD electronics. The ECD/electrometer in the ADA tracer analyzer was exchanged for the ECD/electrometer used in the TGA-4000. The sensitivity of the TGA-4000





CERTIFIED SF<sub>6</sub>  
STANDARD

**Figure 16. Flow system used to test venturi with commercial tracer analyzer ECD.**  
On solenoid valve, "C" denotes the port where flow enters the solenoid, "NO" denotes the normal flow path out of the solenoid, and "NC" denotes the port through which SF<sub>6</sub> flows to the venturi tee when the solenoid switches.

electrometer was ascertained by a zero adjustment potentiometer on the electrometer. Using the venturi to sample room air as shown in Figure 16, the flow of nitrogen through the venturi was carefully adjusted in order to observe the ECD signal as the dilution ratio was varied. It was possible to observe when the flow of air through the inlet orifice reached a point at which oxygen was flooding the detector, indicated by the ECD signal reaching a maximum of 14 volts. It was then necessary to either adjust the zero in order to bring the signal back "on scale", or adjust the nitrogen flow to minimize the oxygen reaching the ECD. At the very high dilution ratios, it was possible to keep the ECD signal "on scale", but the orifice flow was so low that it was extremely unstable and difficult to maintain. Therefore, the dilution ratio was set at the previous value of 31, and the electrometer zero was adjusted. The pulse conditions were varied from the very fast pulses of short duration to very long pulses, and the effect on the SF<sub>6</sub> signal noted. At the smallest, highest frequency pulse widths (50 microsecond period, 1 microsecond width), the 33 ppb SF<sub>6</sub> signal measured from the permeation source was very noisy, and the magnitude was about equivalent to the noise level. At the larger, lower frequency pulse widths (5 ms period, 1 ms width), the signal-to-noise ratio did not improve. These results are similar to data obtained earlier with the Keithley electrometer used in the prototype instrument, and thus no improvement was seen in the measurement of SF<sub>6</sub> in air with the venturi.

#### E. MODIFICATIONS TO PROTOTYPE SYSTEM

It was concluded that measuring SF<sub>6</sub> in air without removing oxygen remains an unrealized goal. In light of this fact, different options for oxygen removal both with and without the venturi were considered. The venturi remains an advantage in this sampling scheme for two reasons: 1) the ability to dilute the ambient oxygen concentration to a fraction of its original level; and 2) the replacement of a power-intensive sampling pump with a nitrogen cylinder. One method of oxygen removal that does not involve combustion with hydrogen (and therefore no production of water) is to combust oxygen with carbon monoxide (1%) to form carbon dioxide. Carbon monoxide in nitrogen would flow through the venturi as the carrier/diluent gas. The combustion reaction would take place downstream of the venturi, and the resulting CO<sub>2</sub> would provide a constant background current against which SF<sub>6</sub> could be analyzed more easily than with oxygen present.

Carbon monoxide was tested for ECD response by introducing a known flow of pure CO into a nitrogen carrier stream. The CO was diluted to 1%, and flowed directly to the ECD. A strong response was noted with the ECD signal rising to 14 volts. Therefore, if 1% CO did not react completely with O<sub>2</sub> to give CO<sub>2</sub>, the SF<sub>6</sub> signal would be obliterated by CO. One percent CO<sub>2</sub> gave a 2.7-volt signal that was easily zeroed out; thus, CO<sub>2</sub> would probably not interfere with SF<sub>6</sub> measurement.

A more viable option is a new tracer analyzer design that utilizes an improved oxygen removal system. This design is based on the commercial Tracer Gas Analyzer. As it is presently configured, the commercial instrument can achieve the sensitivity (4 ppt) required for concentration fluctuation field experiments; the drift rate of the instrument is low enough (3 ppt/min) that it would not interfere with the field measurements; the instrument will easily hold its calibration in a 90-min experimental period; and the

instrument is capable of battery operation (Benner and Lamb, 1985). However, several key improvements can be made in the commercial instrument design which will result in a smaller, less expensive, more efficient, and simpler instrument without sacrificing sensitivity, response time, ruggedness, and stability.

The primary components of the continuous tracer analyzer include the hydrogen reactor (for converting oxygen to water vapor), the Nafion dryer (for removing water vapor from the gas stream), the ECD, and the pump, as shown in Figure 5. Hydrogen would be supplied from a small (1.25" diameter x 8.75" long) metal hydride storage unit. The two-section instrument design proposed in Phase I will be preserved in the new design. A sample head, or "detection module", would contain the sample inlet, sample flow control, hydrogen flow control, catalytic reactor, dryer, and ECD with analog output. This module would be made as small as possible (estimated dimensions of 3"x3"x12") and aerodynamically streamlined with an extended sample "snout" to minimize turbulence around the module or in the vicinity of the sample inlet. A larger ground unit, or "support module", would house the hydrogen storage unit, sample pump, power source, and data acquisition system. It is envisioned that each ground unit would support multiple detection modules.

#### **F. PHASE II APPROACH**

The development of the prototype tracer analyzer would involve the following tasks:

- o **Investigation of Different Reactor Designs and Operating Conditions.** The hydrogen reactor in its present configuration has a large pressure drop. Reducing the pressure drop will allow reduction in the size and power consumption of the pump. Different forms of the catalyst (e.g., palladium wool, rolled palladium foil, platinized quartz frits) and designs of the hydrogen reactor will be investigated in order to decrease the pressure drop. This may also cause an increase in the sample flow rate, which will result in an improved time response.
- o **Modification of the ECD and Adjustment of the Pulse Period.** A smaller ECD design, a dual ECD configuration, the use of scandium tritide instead of titanium tritide, heating the ECD (to about 200°C), and changing the pulse period are design modifications that could improve the stability, decrease the detector dead volume, provide the capability to automatically clean the detector, and reduce or eliminate the temperature dependence of the ECD. A heated ECD could also eliminate the need for a dryer, reducing the response time of the instrument by decreasing the dead volume.
- o **Improvement of the Nafion Dryer.** If it is not possible to eliminate the dryer, the use of ambient air as the dryer purge gas instead of nitrogen will eliminate the need for a nitrogen cylinder. Also, using the heat generated from the catalytic reactor to heat the dryer inlet, as well as increasing the insulation on the dryer, would conserve power. The addition of resistance

wires on the Nafion tubing to monitor humidity and verify dryer performance before breakthrough of water vapor to the ECD occurs would help to maintain detector stability.

- o **Optimization of System Operation.** Parameters such as sample flow rate and hydrogen/sample flow ratio will be optimized to reduce the instrument response time. Smaller diameter tubing will reduce the dead volume in the flow system, which will also reduce the response time.
- o **Use of a Microcontroller to Automate Instrument Operation.** A commercial microcontroller that is currently being tested by ADA Technologies is a likely candidate to control and monitor flows, temperatures, and ECD signal.
- o **Laboratory Evaluation of the Prototype Instrument Flow System.** The components which were tested individually in the first five tasks will be assembled as the prototype flow system. An SF<sub>6</sub> calibration, calibration stability check, response frequency experiment, and drift monitoring will be performed.
- o **Fabrication of Several Prototype Instruments for Field Use.** Based on the results of the laboratory experiments, the prototype instrument components will be modified as needed to meet the required performance specifications. The components will then be replicated and assembled in several two-section field instruments, which will each include a data acquisition system. A schematic diagram of the prototype tracer analyzer is shown in Figure 17.
- o **Field Evaluation of the Prototype Tracer Analyzer.** The prototype tracer analyzers will be tested in an actual concentration fluctuation field experiment.
- o **Development of a Final Tracer Analyzer Design.** Based on the results of the field experiments, modifications will be made to the prototypes as necessary to optimize their performance in the field.

A potential Phase III relationship is being pursued with ScienTech, Inc., due to its expertise in tracer gas instrumentation. Mr. John Frame, President of ScienTech, will consult on the Phase II program.

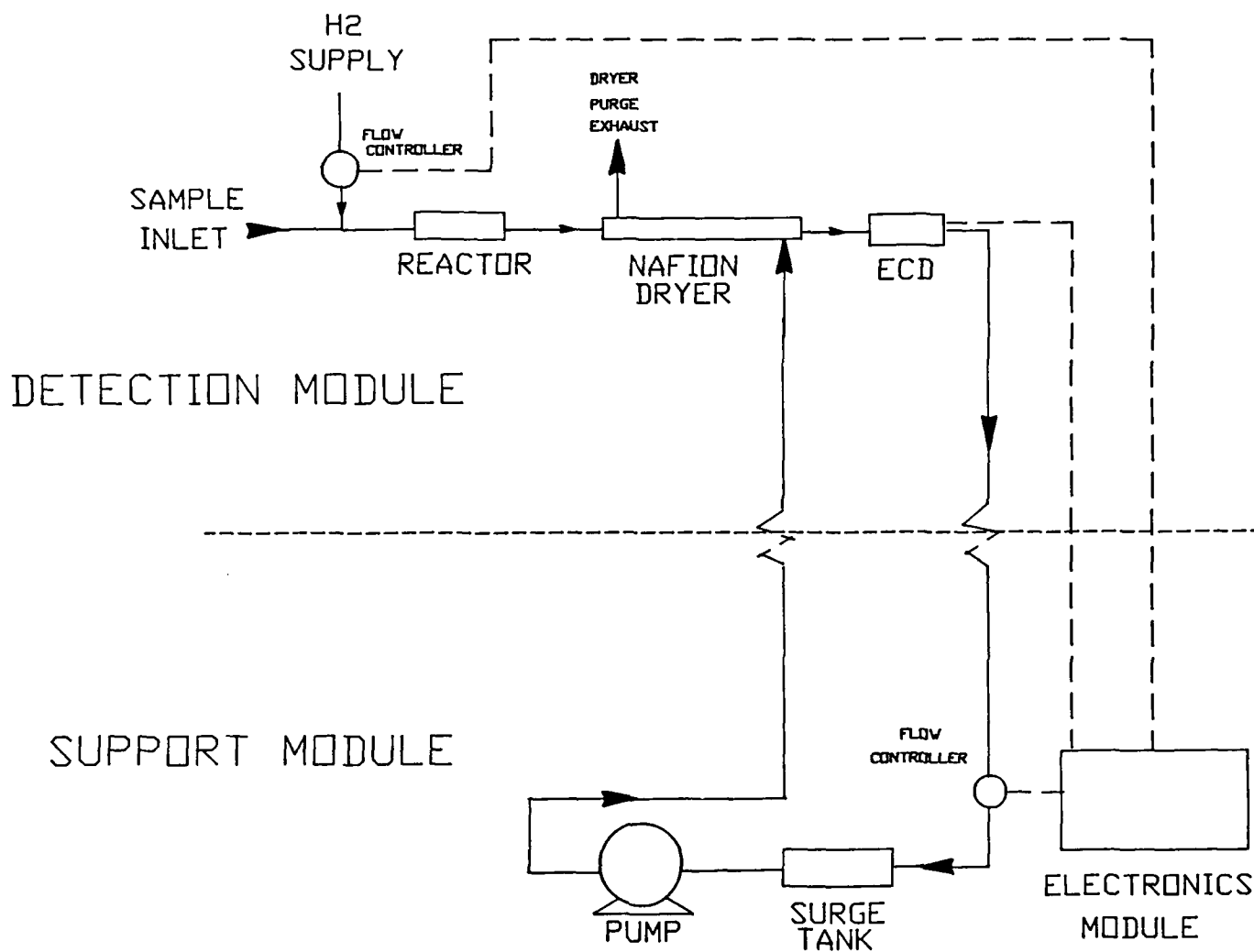


Figure 17. Phase II prototype tracer analyzer.

## **G. CONCLUSIONS AND ESTIMATE OF TECHNICAL FEASIBILITY**

A new measurement method for atmospheric tracer compounds was developed and tested during this Phase I program. The new technology incorporates the electron-capture detector in a venturi-sampling flow scheme. No pump is required to operate the flow system; the venturi serves the dual function of drawing the air sample into a nitrogen carrier stream and diluting the air such that the ambient oxygen concentration is greatly reduced. Oxygen is not destroyed before the air sample containing the tracer material reaches the ECD. This method did not demonstrate feasibility, due to inability to overcome the oxygen interference sufficiently to achieve the desired detection limit for SF<sub>6</sub> of 200 ppt. Based on the results of the Phase I study, the following conclusions can be made regarding the tracer device:

1) **The venturi flow system successfully diluted and transferred an air sample to the ECD.** The venturi was characterized over a range of nitrogen flows, and was found to provide dilution ratios in the range specified in the Phase I proposal.

2) **SF<sub>6</sub> was measured when the pure gas was injected near the venturi orifice.** The SF<sub>6</sub> concentration was not known, but was probably quite high. The signal was very sharp.

3) **SF<sub>6</sub> was measured at 32 ppb with the venturi sampling system.** This concentration was determined to be the approximate limit of detection of the method.

## IX. REFERENCES

- Baxter, R.A. (1982). "A Portable Continuous SF<sub>6</sub> Analyzer Suitable for Airborne Platforms." Proceedings from the Air Pollution Control Association Specialty Conference on In-Situ Air Quality Monitoring from Moving Platforms, San Diego, CA.
- Benner, R.L. and B. Lamb (1985). "A Fast Response Continuous Analyzer for Halogenated Atmospheric Tracers." *J. Atmos. Oceanic Technol.* 2, 582-589.
- Blevins, R.D. (1984). **Applied Fluid Dynamics Handbook**. Van Nostrand Reinhold Company, New York.
- Deardorff, J.W. and G.E. Willis (1984). "Groundlevel Concentration Fluctuations from a Buoyant and a Non-Buoyant Source within a Laboratory Convectively Mixed Layer." *Atmos. Environ.* 18, 1297-1309.
- Durham, M.D. (1983). **Operators Manual: The DRI Fine Particle Dilution System**. March.
- Hanna, S.R. (1984). "Concentration Fluctuations in a Smoke Plume." *Atmos. Environ.* 18, 1091-1106.
- Hanna, S.R. (1986). "Spectra of Concentration Fluctuations: The Two Time Scales of a Meandering Plume." *Atmos. Environ.* 20, 1131-1137.
- Lamb, B.K. (1980). "The W.S.U. Continuous SF<sub>6</sub> Analyzer." Prepared for Regional Field Studies Office, Environmental Science Research Laboratory, Research Triangle Park, NC. Department of Chemical Engineering, Washington State University, Pullman, WA.
- Lee, R. (1984). Personal communication. Battelle Northwest Laboratories, Richland, WA.
- Niemeyer, L.E. and R.A. McCormick (1968). "Some Results of Multiple-Tracer Diffusion Experiments at Cincinnati." *J. Air Poll. Contr. Assoc.* 18, 403-405.
- Pasquill, F. (1983). **Atmospheric Diffusion**. John Wiley and Sons, New York, NY, pp. 181-183.
- Peterson, H.G., B.K. Lamb, and D.E. Stock (1988). "Plume Concentration and Velocity Fluctuations During Convective and Stable Conditions." Preprint from Eighth Symposium on Turbulence and Diffusion, San Diego, CA, Apr. 26-29, 1988.
- Poole, C.F. and A. Zlatkis (1981). "The Design and Operation of the Electron-Capture Detector" in **Electron Capture: Theory and Practice in Chromatography**, A. Zlatkis and C.F. Poole, eds. Elsevier Scientific Publishing Company, New York, NY, pp. 13-26.

Ramsdell, J.V., Jr. and W.T. Hinds (1971). "Concentration Fluctuations and Peak-to-Mean Concentration Ratios in Plumes from a Ground-Level Continuous Point Source." *Atmos. Environ.* 5, 483-495.

Simmonds, P.G., A.J. Lovelock, and J.E. Lovelock (1976). "Continuous and Ultrasensitive Apparatus for the Measurement of Air-Borne Tracer Substances." *J. Chromat.* 126, 3-9.